NASA CR-66394

FINAL REPORT

DEVELOPMENT OF PHASE-CHANGE COATINGS FOR USE AS VARIABLE THERMAL CONTROL SURFACES

R. N. Griffin and B. Linder

Prepared under Contract NAS1-5330 by

Materials Sciences Section
Space Sciences Laboratory
Missile and Space Division
General Electric Company
Box 8555, Philadelphia, Pennsylvania 19101

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

GENERAL ELECTRIC
COMPANY

VALLEY FORGE SPACE TECHNOLOGY CENTER (MAIL: P. O. BOX 8555, PHILA., PA. 19101), TEL. (215) 962-2000

MISSILE AND
SPACE DIVISION

SPACE SCIENCES
LABORATORY

September 18, 1967

Re: Contract NAS1-5330

Final Report

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Very truly yours,

E.A. Blum
Contract Administrator

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FOREWORD

This document, "Development of Phase-Change Coatings for Use as Variable Thermal Control Surfaces," is the final report on the program conducted during the period of December 9, 1965 to December 9, 1966 for the National Aeronautics and Space Administration under Contract NAS1-5330. The program was monitored by Mr. Warren Kelliher of the Langley Research Center of that agency. Dr. R. N. Griffin of the Space Sciences Laboratory, General Electric Missile and Space Division, was the principal investigator.

The authors wish to acknowledge the contributions of Dr. D. G. Flom in helpful discussions throughout the program and in suggested revisions in the manuscript.

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DEVELOPMENT OF PHASE-CHANGE COATINGS FOR USE AS VARIABLE THERMAL CONTROL SURFACES

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SUMMARY

Variable thermal control coatings employing the so-called phase-change principle were first developed and demonstrated at NASA, Langley Research Center. As an aid to understanding of the principles involved in such coatings, some of the results of the research conducted at Langley are presented herein with the permission of Mr. Warren Kelliher, the technical monitor of Contract NAS 1-5330.

When such coatings are in the transparent state, the pigment and binder are mutually soluble, forming a homogeneous single phase solution. As the temperature is lowered, the saturation temperature for the particular composition of binder and pigment is reached and a portion of the pigment comes out of solution to form a separate phase. However, since this saturation temperature is at or below the melting point of the pigment, crystals of solid pigment are formed dispersed throughout the binder. Thus, when the phase-change coating is in the diffuse state, it is a heterogeneous dispersion of two phases, a pigment-plasticized amorphous binder and solid crystalline particles of pigment.

The research supported on Contract NAS1-5330 was designed to develop a practical coating system utilizing this concept that would be useful as a self-thermostatic thermal control system.

Over two hundred formulations were investigated in the development of phase-change coatings for practical application to spacecraft. From these formulations a better understanding of the necessary materials properties was obtained, an understanding was gained of the mechanism of operation of phase-change coatings, and practical coating systems were developed.

It was shown that the plasticity of the coating affects the rate of recovery from the transparent to the "opaque" state.

At least in some systems there is no unique "phase-change" temperature, but rather a constant change of absorptance with temperature over a temperature range of about 20°C. There is, however, a temperature at which a phase-change coating undergoes a rapid change of absorptance. This temperature, is, in the best coatings, at or just below the melting point of the pigment.

A phase-change coating system was developed which can be applied by brushing or spraying. It has approximately a two-fold change in absorptance between 25° and 50°C, is stable to 10^3 thermal cycles in vacuum, and is essentially unaffected by exposure in vacuum to 100°C, 1000 equivalent sun-hours of ultraviolet, and 100 Mrad x-radiation.

I. INTRODUCTION

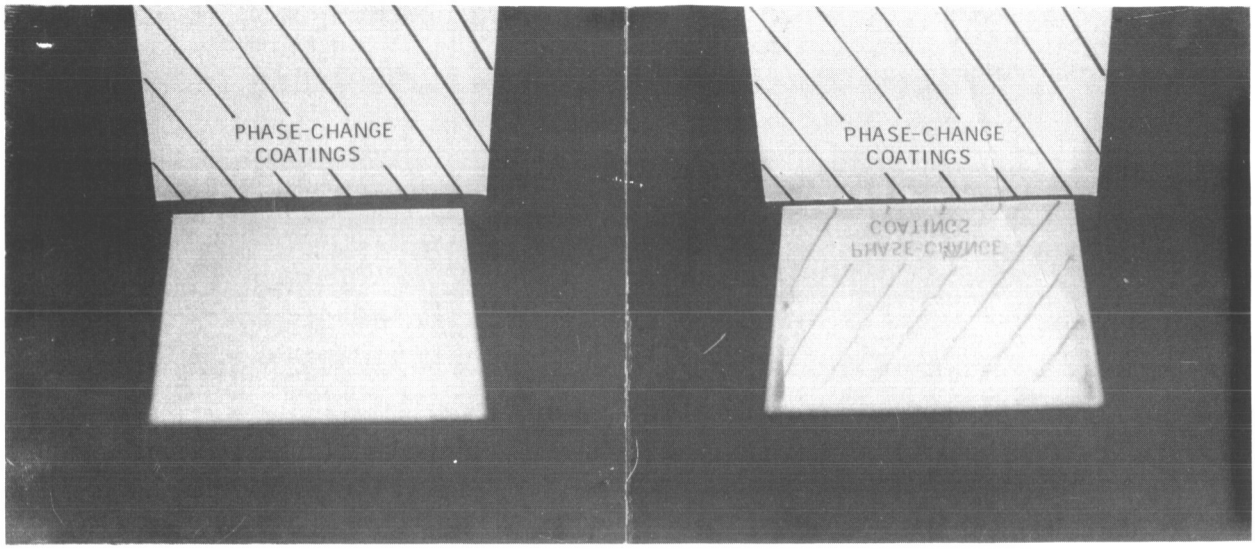
The design of long-lived, reliable spacecraft requires that internal vehicle temperatures be maintained as constant as practical. Construction of a nearly isothermal space vehicle, especially when the heat flux is not constant, requires an elaborate thermal control system. In the past, such vehicles have been designed with thermally-actuated mechanical shutters. These shutters would either absorb or reflect sunlight depending on the temperature of the vehicle.

Recently the NASA Langley Research Center devised a type of thermal control coating which performs the same function as the currently-used shutters, but does not require any moving or mechanical parts. The principle of operation is this type of coating is the temperature-dependent solubility of a pigment in a polymeric binder. The coating thus undergoes a temperature-dependent reversal in transparency, so that at low temperatures it is opaque and absorbing, while at elevated temperatures it is transparent, thereby exposing a reflecting substrate. This contractual research program was designed to develop a practical coating system utilizing this concept that would be useful as a self-thermostatic thermal control system.

A. Objective of Work

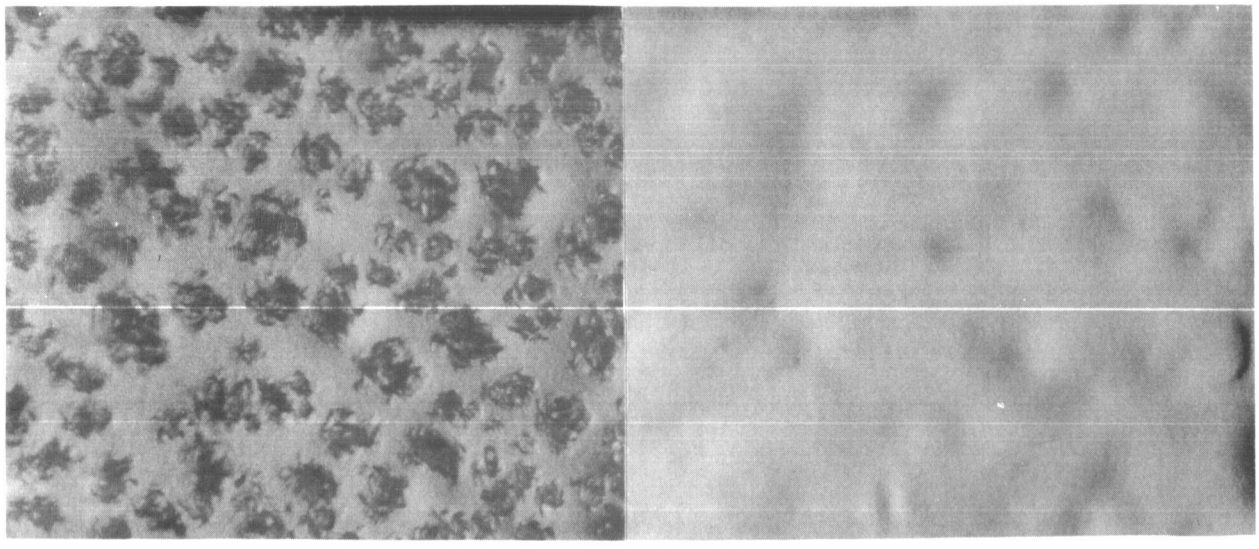
Model systems developed by the Spacecraft Materials Section of the NASA Langley Research Center have demonstrated a means of producing a variable thermal control coating. The term "phase-change coating" was coined to describe this class of material. The objective of the present work was to develop coating systems, using the phase-change concept, which would be stable to the vacuum, the ultraviolet radiation, and the high energy radiation associated with the space environment. These coatings were also required to have the requisite physical, mechanical, and optical properties necessary for practical application to spacecraft.

B. Demonstration of the Operation of Phase-Change Coatings



Low-Temperature,
Opaque State

High-Temperature,
Transparent State



Photomicrograph, Low-
Temperature State

Photomicrograph, High-
Temperature State

II. LIST OF SYMBOLS

α_s	solar absorptance
ϵ	emittance
Mrad	megarads
ESH	equivalent sun hours of ultraviolet irradiation
DP	dioctadecyl phosphite
PVB	poly(vinyl butyral)
T	absolute temperature
w	watt(s)
RT	room temperature
ET	elevated temperature
B98, B76, B90	types of poly(vinyl butyral) sold by Monsanto Co. under the trademark "Butvar"

III. EXPERIMENTAL

A. Irradiation of Binders

In its simplest form a phase-change coating consists of a pigment which is partially soluble in a binder or vehicle. The first phase of the work therefore consisted of the evaluation of eight potential binders, poly(vinyl fluoride), poly(vinylidene fluoride), Owens Illinois Glass Resins 100, 650, 900, and 901, General Electric Silicone Products Dept. Experimental Resin #391-15-170 (formerly called "PJ113")*, and poly(vinyl butyral). The initial choice of potential binder materials was made primarily by consideration of probable stability to the space environment. It was known that phenyl silicones such as Glass Resins 100 and 901 would not be as stable to ultraviolet exposure as the methyl silicones, but other considerations made it seem worthwhile to include them. Also, experimental formulations were made with RTV 602, but it was felt that enough stability data already exist on this material so that a reinvestigation was not warranted unless this proved to be the final choice of binder.

Potential binders for use in phase-change coatings were screened by an examination of their relative stabilities to ultraviolet and x-radiation in vacuum. Irradiations were conducted in the apparatus shown in Figure 1. The vacuum system has an adsorption fore-pump and a triode ion pump. It normally operates at about 1×10^{-8} torr without bakeout. The ultraviolet source was a Hanovia high-pressure xenon lamp powered by a Christie Electric Co. constant current supply. The light was filtered through 5 cm of Harleco "ultra-pure" water to remove light above 0.9μ. It entered the vacuum chamber through a sapphire window. Intensity measurements were made with a calibrated Eppley copper-constantan thermopile. X-rays were supplied by a G.E. XRD-6 generator operated at 4.5 ma and 46 kv. Voltage ripple was less than 3%, and current was regulated to ± 0.2 ma. The x-ray intensity at the sample position was determined by dimethoxy diphenyl-bisazobis-8-amino-1-naphthol-5, 7-disulfonic acid dye dosimetry using the Co^{60} calibration curve of Henley and Richman.[1] This method was chosen because of the physical and chemical similarity of dosimeter and samples and because of the limited space available at the sample position. The samples consisted of 1 inch diameter discs coated with vapor-deposited aluminum over which was applied a nominal 5 mil coating of the candidate binder. The normal procedure was to place five or more identical samples in the chamber and to evacuate the system overnight. System pressure at the beginning of irradiation was never higher than 6×10^{-7} torr and generally was below 1×10^{-7} torr. Some pressure rise was noted at the beginning of

* PJ113 and silicone 391-15-170 are the same material except that the latter is obtained as a prepolymer and the former was made from monomers. Both designations are carried throughout this report to minimize confusion between the old and the new terminology.

Figure 1. Vacuum Irradiation System

each irradiation. The largest increase was noted with poly(vinyl butyral), a rise from 5×10^{-8} torr to 1×10^{-6} torr. This was probably due largely to liberation of trapped solvent and low molecular-weight materials since prolonged exposure in vacuum prior to irradiation minimized the pressure rise that was observed when irradiation was started.

Absorptance measurements were made on the samples after removal from the vacuum chamber. While measurements made in this fashion cannot detect oxygen-sensitive radiation damage, the errors introduced are not likely to be as important in the cases studied in this work as they are in coatings pigmented with metal oxides or other semi-conductor pigments.[2]

From these studies it was concluded that both poly(vinyl butyral) and the silicone PJ 113(391-15-170) were sufficiently stable to be used as binders in this program. Some materials originally considered as potential binders were not irradiated since they had previously been eliminated from consideration because of high temperature cure cycles. These materials included poly(vinylidene fluoride) and Glass Resins 650, 900, and 901. The results of irradiations of binders are summarized in Tables I through IV and Figures 2 through 6.

B. Other Criteria for Binder Selection

As the work progressed, it became evident that stability was not the only criterion for selection of binders. Others include the cure cycle, the solvent power*, the plasticity of the binder, and the tendency of pigments to migrate to the surface of the binder.

The cure cycle of the binder proved to be the major stumbling block for the majority of the binders considered in this program. Both poly(vinyl fluoride) and poly(vinylidene fluoride) must be sintered at high temperature in order to produce a coherent, transparent film. (This, of course, is not really a "cure", but the effect is the same.) The four Glass Resins must be cured at high temperatures. All pigments investigated either vaporized or degraded during the cure of these resins.

The ability of the binder to dissolve the pigment is important because it determines the maximum concentration of pigment which can form a homogeneous solution at the phase-change temperature. Hence, it is one of the factors that determine the opacity of a coating at low temperatures. But even more important than solvent power itself is the constancy of solvent power both before and after exposure of the coating to thermal cycling, irradiation, and long standing. For instance, some of the formulations made with silicone

* Solvent power or solvency is a loosely defined term used to describe the ability of a solvent to dissolve a particular solute.

TABLE I. EFFECT OF IRRADIATION ON SILICONE PJ 113 (391-15-170) SAMPLES

Sample Designation	Exposure		Solar Absorptance	
	Ultraviolet ESH	X-ray Mrad	Initial	Final
Bare aluminum	None	None	.12	--
6-1	17	1	.16	.16
6-2	172	10	.16	.17
6-3	860	50	.16	Destroyed in test
6-4	1720	100	.16	.18
6-5	1000	100	.18	.20

System pressure:

initial - 1×10^{-7} torr

highest - 1.5×10^{-7} torr

final - 2×10^{-8} torr

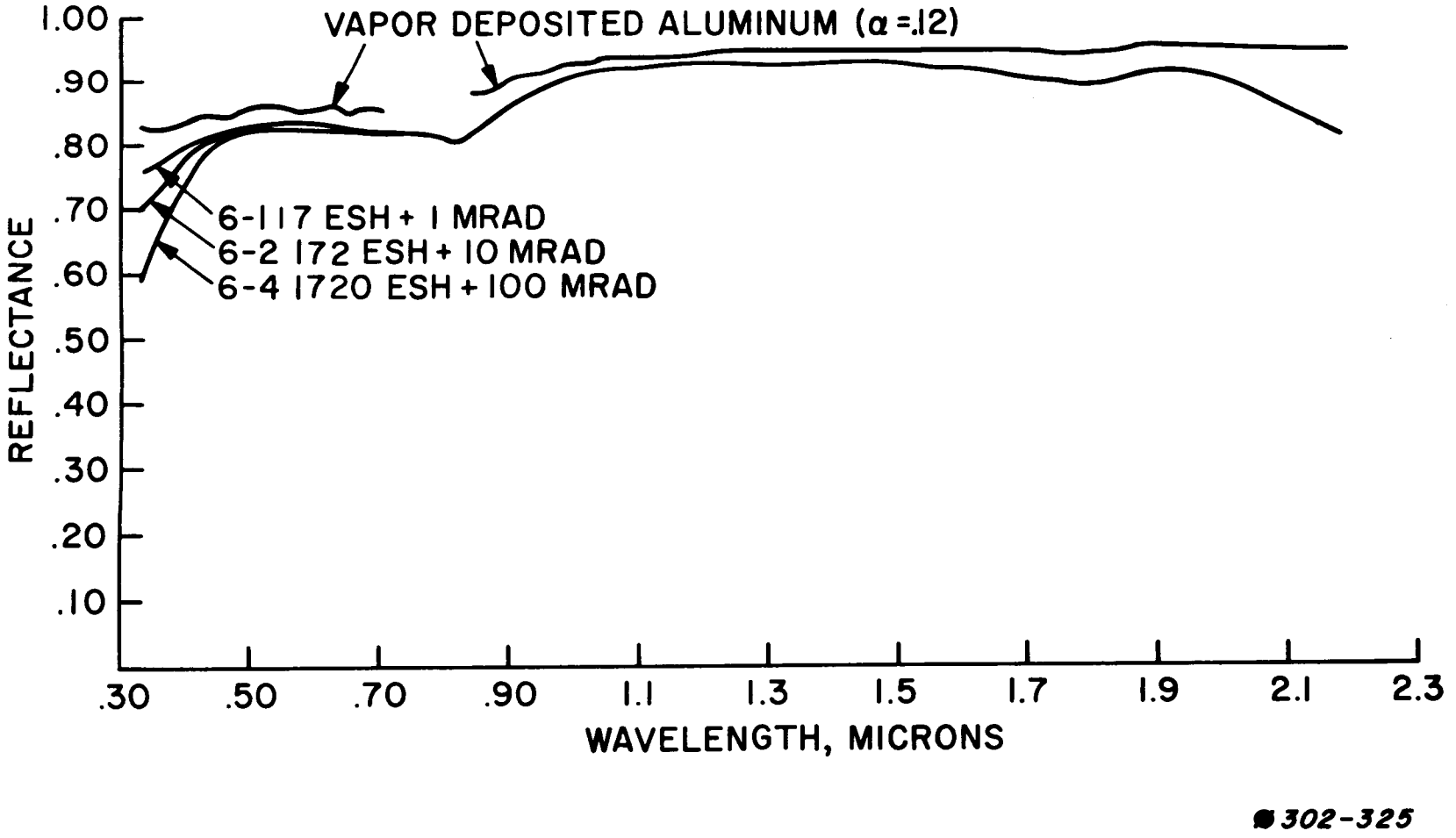


Figure 2. Effect of Irradiation on the Spectral Reflectance of Silicone PJ 113(391-15-170) on Aluminum

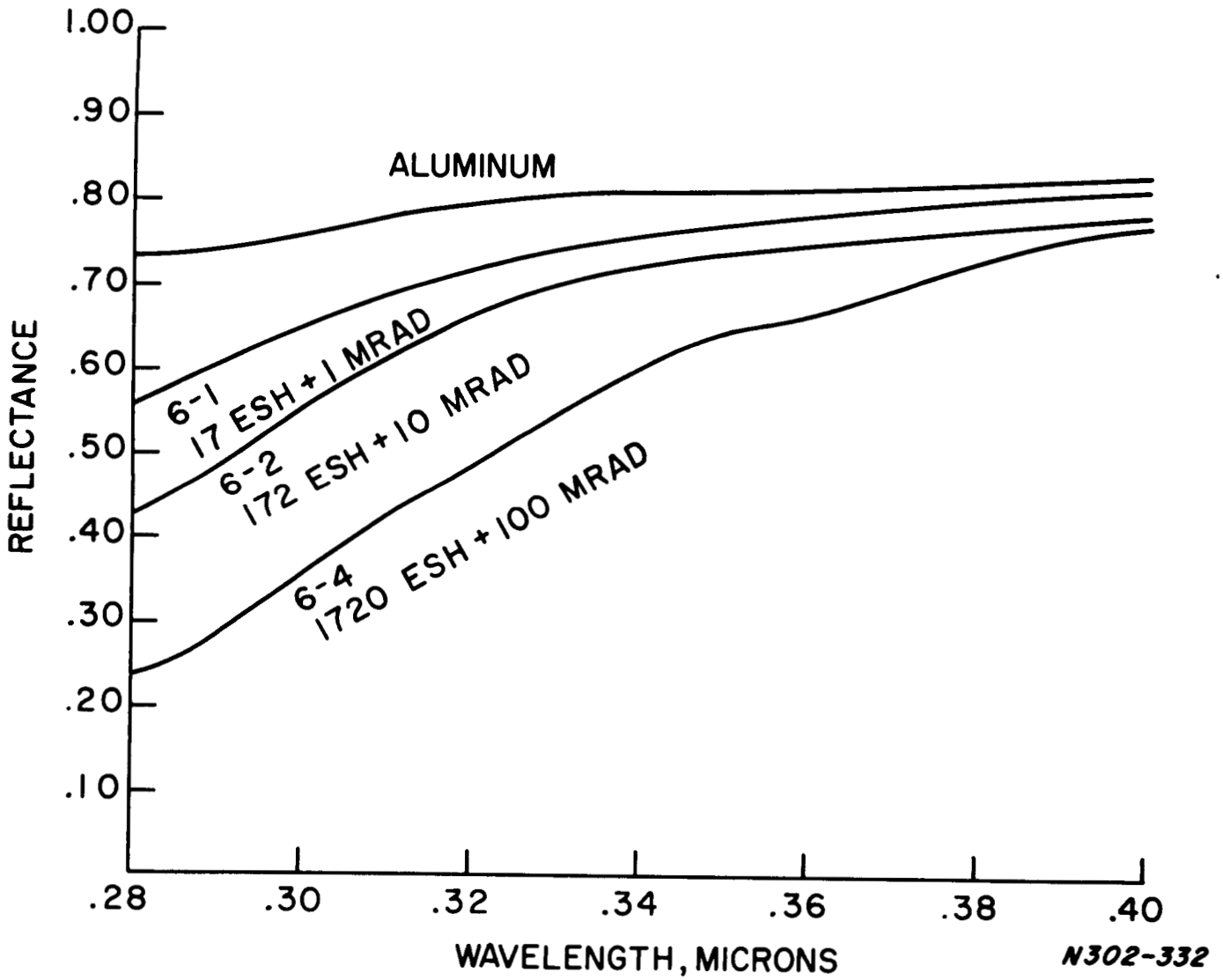


Figure 3. Effect of Irradiation on the Ultraviolet Reflectance of Silicone PJ 113(391-15-170) on Aluminum

TABLE II. EFFECT OF IRRADIATION ON POLY(VINYL BUTYRAL)

Sample Designation	Exposure		Solar Absorptance	
	Ultraviolet ESH	X-ray Mrad	Initial	Final
8-1	10	1	.18	.19
8-2	100	10	.19	.20
8-3	500	50	.18	.20
8-4	1000	100	.18	.20

System pressure:

initial - 5×10^{-8} torr

highest - 1×10^{-6} torr

final - 2×10^{-8} torr

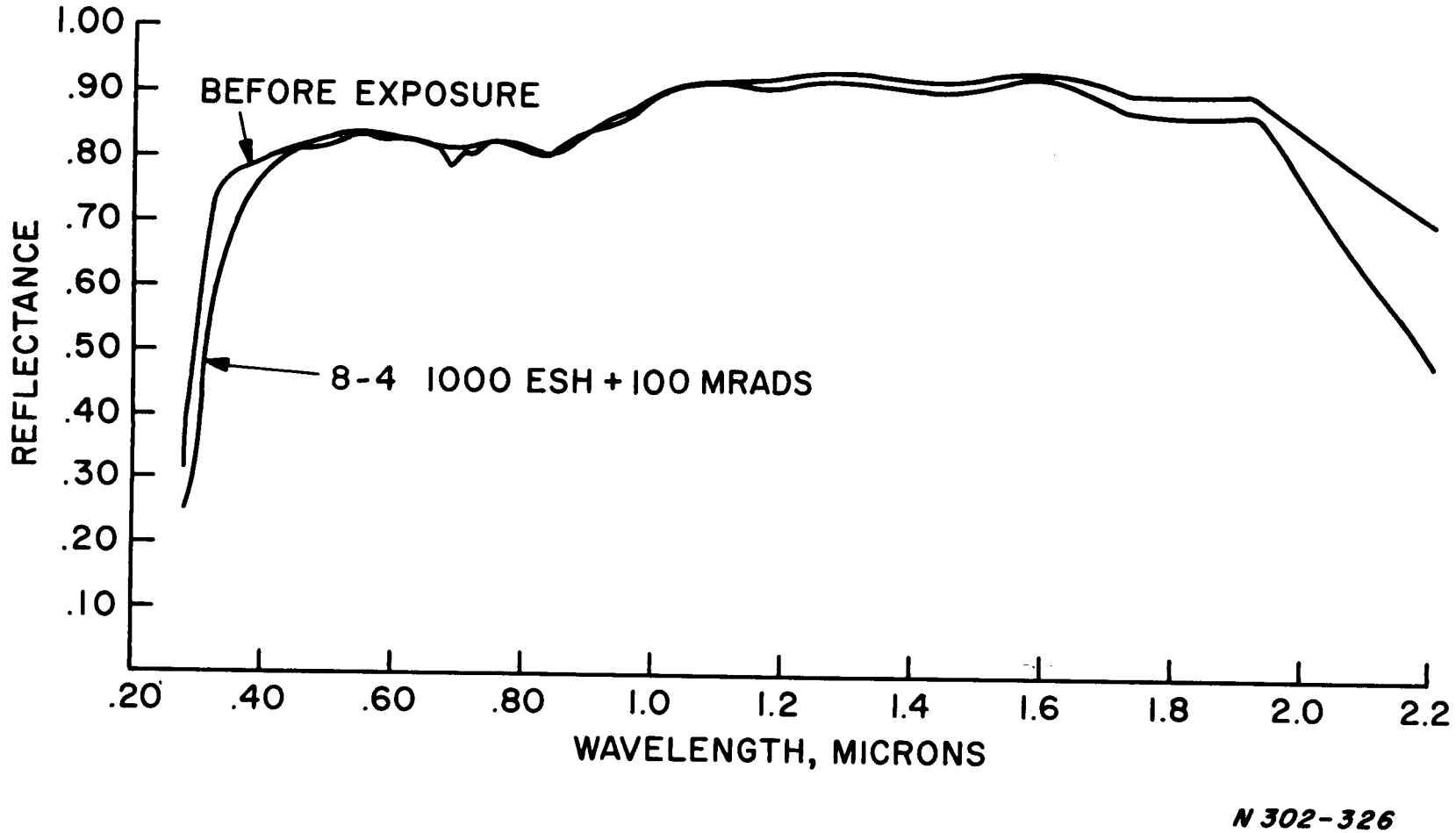


Figure 4. Effect of Irradiation on the Spectral Reflectance of Poly(vinyl butyral) Sample 8-4

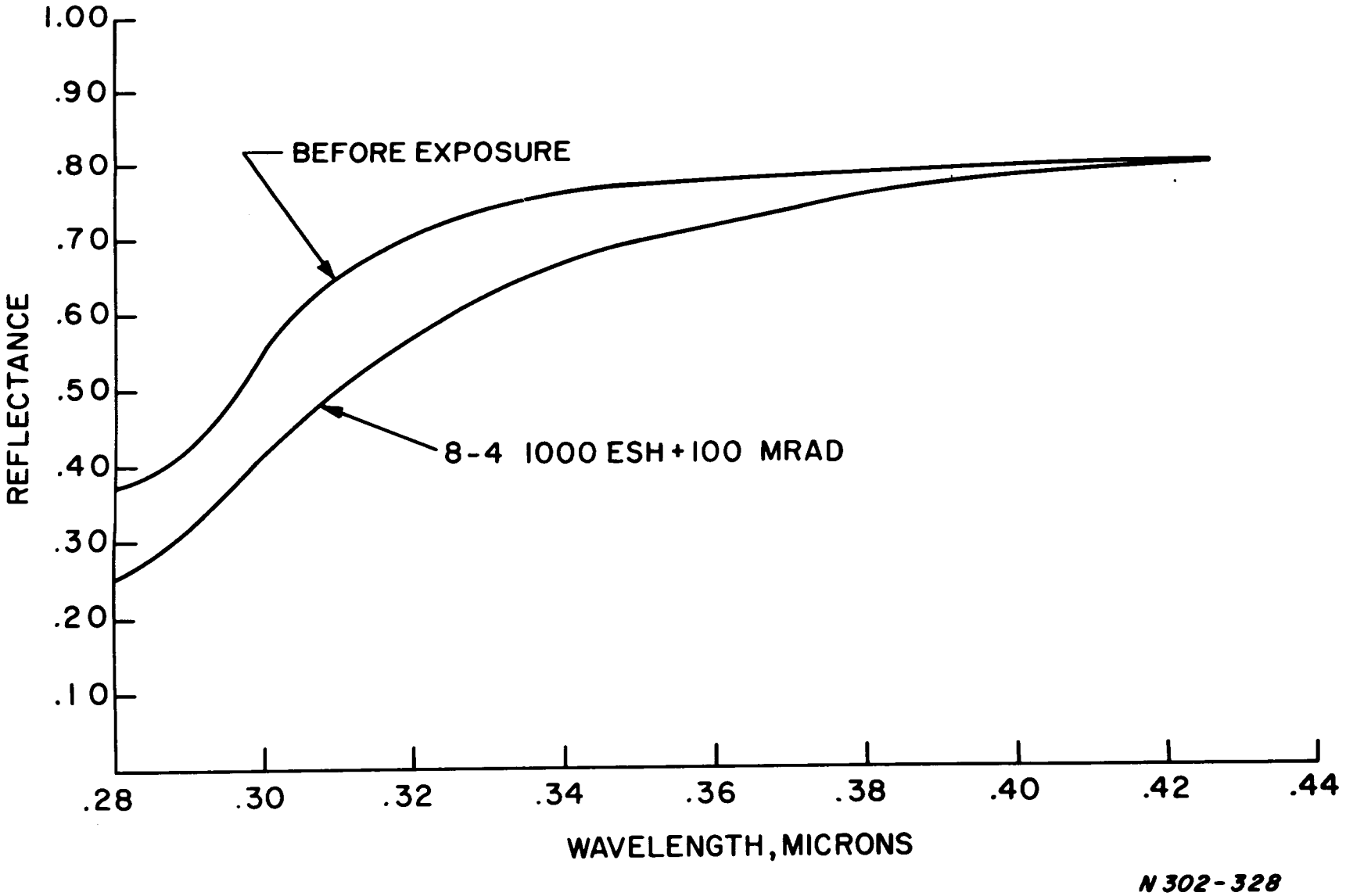


Figure 5. Effect of Irradiation on Ultraviolet Reflectance of Poly(vinyl butyral) Sample 8-4

TABLE III. EFFECT OF IRRADIATION ON SAMPLES OF "GLASS RESIN" 100

Sample Designation	Exposure		Solar Absorptance	
	Ultraviolet ESH	X-ray Mrad	Initial	Final
18-1	10	1	.19	.20
18-2	100	10	.19	.23
18-3	500	50	.19	Destroyed in test
18-5	1000	100	.19	Destroyed in test

System pressure:

initial - 6×10^{-7} torr

highest - 6×10^{-7} torr

final - 2×10^{-8} torr

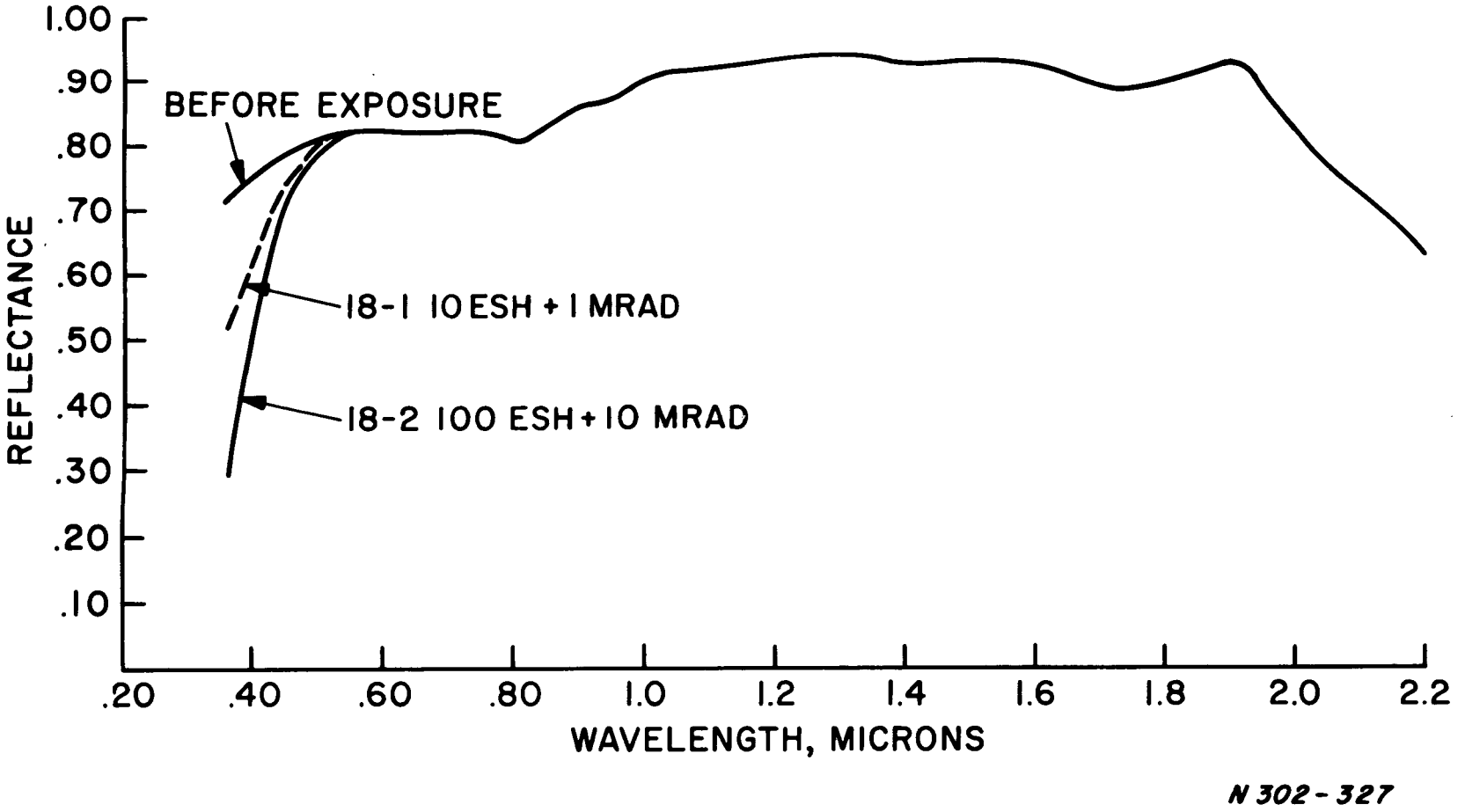


Figure 6. Effect of Irradiation on Samples of "Glass Resin" 100

TABLE IV. EFFECT OF IRRADIATION ON SAMPLES OF POLY(VINYL FLUORIDE)

Sample Designation	Exposure		Solar Absorptance*	
	Ultraviolet ESH	X-ray Mrad	Initial	Final
18-D1	10	1	.24	.24
18-D2	100	10	.17	.19
18-D3	< 500	50	.21	.25

*Measurements made with Gier Dunkle Portable Reflectometer and therefore should be considered as relative measurements.

System pressure:

initial - 6×10^{-8} torr

highest - 6×10^{-8} torr

final - 2×10^{-8} torr

PJ113 (391-15-170) contained about 5% pigment. Such coatings were quite opaque when cold and very transparent when warm. However, after 10^3 thermal cycles or after standing at room temperature for about a month these coatings became permanently opaque--lost their ability to undergo a "phase-change". This was attributed to further cross-linking and a consequent change in the solvent power of the binder. It was found that the fully cured resin could dissolve only about 1% of most pigments, not enough to produce reasonable opacity in the low temperature state.

The importance of plasticity of the binder gradually became evident during the course of the work. Plasticity itself apparently does not affect the equilibrium properties of a coating, but does affect the rate of approach to equilibrium. It was noted that some coatings made with poly(vinyl butyral) recovered from their high to their low temperature state within a minute or so when the coatings were new. But after repeated thermal cycling in vacuum, these same coatings required an hour or more to regain their low temperature opacity. The first clue to the explanation of this behavior came from an investigation of one of the model coatings developed at NASA Langley. This coating recovers its opacity almost instantaneously on cooling, yet employs a type of polystyrene as binder, so at room temperature it has a very low degree of plasticity. It was noted, however, that above the phase-change temperature this coating becomes extremely soft, almost fluid. When the coating was cooled slowly it was noted that the recovery of opacity occurred prior to solidification of the coating. From this observation it was concluded that the apparent "fatiguing" of the poly(vinyl butyral) coatings might be due to removal of traces of solvent during heating in vacuum. With the removal of solvent the coating lost plasticity and the rate of recrystallization of the pigment was diminished. The validity of this reasoning was demonstrated when the addition of plasticizer (Resoflex R-296) to the poly(vinyl butyral) formulations eliminated the "fatiguing" due to thermal cycling in vacuum.

Studies were conducted independently of this contract at NASA, Langley Research Center on a model phase-change coating system consisting of paraffin in styrene-vinyl toluene copolymer. It was found that when the percentage of paraffin in the coating was increased beyond the 30% level, the saturation temperature exceeded the freezing point of the paraffin by more than 20°C. As a result, when these coatings were cooled, the paraffin that separated from the solution was still in liquid form and tended to condense and migrate to the surface of the coating due to the density differential. Satisfactory phase-change coatings therefore require a saturation temperature below the freezing point of the pigment to avoid this problem.

Using a number of different pigments in combination with the styrene-vinyl toluene copolymer, it was found that those blends having a saturation temperature much lower than the freezing point of the pigment did not form the relatively opaque coatings that were formed by blends that had a saturation temperature close to the freezing point temperature. These coatings were

quite translucent and the opacity was greatly dependent upon the thermal history of the sample, i.e., number of thermal cycles and cooling rate. Since this copolymer has a glass transition temperature of 50-56°C, a plasticizer was added to the blends in order to lower this glass temperature below the phase-change temperature range of the coatings. While this alleviated some of the dependency of the opacity of the coatings on thermal history, maximum opacity was achieved only when the saturation temperature and pigment freezing point were approximately the same. It therefore appears that two criteria are required to obtain maximum opacity and negligible dependency on thermal history: (1) The glass transition temperature of the binder must be below the phase-change temperature range of the coating. The crystallization of the pigment must not be hindered by the rigidity of the polymeric structure, and sufficient internal mobility and flexibility must be present to allow pigment separation and coalescence. (2) The saturation temperature of the pigment-binder solution and the freezing point of the pigment must be as close as possible. The pigment as it separates out must not crystallize too quickly but be allowed to coalesce, permitting nucleation of a satisfactory crystal structure.

C. Formulation of Phase-Change Coatings

In the course of this work, approximately 205 coating formulations were made. These formulations represent variations of about 90 combinations of pigment, binder, and additives such as plasticizers and nucleating agents. While much of the formulation work in the early part of the program made use of silicone binders, the later work was concerned almost exclusively with formulations made from poly(vinyl butyral). The reasons for the emphasis on poly(vinyl butyral) have been discussed in Sections A and B above.

The formulations investigated are listed in Appendix A with appropriate comments. More complete discussion of the system, dioctadecyl phosphite (DP) in poly(vinyl butyral) (Butvar B98) is warranted.

A number of formulations were made which consisted of dioctadecyl phosphite in poly(vinyl butyral). Significant differences in behavior were noted as a result of differences in purity of the dioctadecyl phosphite, nature of the plasticizer (when used), presence of nucleating agents, and methods of incorporation of the latter.

The dioctadecyl phosphite as received was a hard, off-white mass. When it was used in this condition, it produced coatings which were relatively satisfactory except that recovery from the transparent to the "opaque" state sometimes required a period of hours. (As used here, "recovery" refers to the visual impression of the coating at room temperature. As discussed in Section E, this does not mean that all instrumentally-detectable changes were complete.) Recrystallization of the dioctadecyl phosphite from methanol

produced a white, free-flowing powder. This material, however, exhibited the same characteristics in coatings as the original material. When the dioctadecyl phosphite was recrystallized from petroleum ether, it was again white and free-flowing. Coatings made from this material had greatly improved recovery rates, reaching the "opaque" state in a matter of minutes.

Some further improvement in recovery rates was achieved by incorporation of about 1% of finely divided silica (Cab-O-Sil) in the formulation. The improvement due to Cab-O-Sil was not very consistent until it was found that better dispersion of the silica was achieved if the silica was ground in solvent on a ball mill prior to mixing in the coating formulation. The well-dispersed silica, however, raised the high-temperature absorptance of coatings by ~.03 - .04, so the concentration of silica was decreased to 1/4%.

Even then, a noticable decrease in the rate of recovery was noted after prolonged thermal cycling in vacuum. As is discussed in Section A, this problem was solved by the addition of a plasticizer (Resoflex-R296) to the formulation. The coating formulation on which most of the experiments such as radiation effects (Section G) and recovery rates (Section E) were performed consisted, therefore, of 30% dioctadecyl phosphite*, 20% Resoflex R296, and 1/4% Cab-O-Sil in Butvar B98.

Finally, some dioctadecyl phosphite was zone-refined by the Spacecraft Materials Section of NASA, Langley. When the zone-refined material was used as pigment, recovery rates were even faster than when recrystallized material was used and changes in absorptance occurred at lower temperatures (Section E). In this case, no benefit was found from inclusion of Cab-O-Sil in the formulation, and the best coating formulation was found to consist of 30% zone-refined dioctadecyl phosphite and 20% Resoflex R296 in Butvar B98.

Since the degree of purity of the DP obviously affects the recovery kinetics and to some extent the room temperature reflectivity, a comparison was made of the melting point and index of refraction for various samples. The effect of purification methods on physical properties of dioctadecyl phosphite is shown in Table V.

Since it was felt that the best protective layer would be one in which the pigment was relatively insoluble, four possibilities were considered. A layer of silicone or a layer of poly(vinyl butyral) cross-linked with hexamethoxymethylmelamine (Cymel 300) or toluene di-isocyanate might be applied, or the phase-change coating might be applied to a film of poly (vinylidene fluoride) which would become the outer layer of a tape. The toulene di-isocyanate was not received in time to be included in the investigation, and

* Percentage compositions refer to number of grams of material per 100 grams of binder. In terms of total solids the above formulation contained 20% dioctadecyl phosphite.

several attempts to make coatings on poly(vinylidine fluoride) films were unsuccessful. But both Cymel-crosslinked poly(vinyl butyral) and silicone PJ 113(391-15-170) were successfully applied to coatings of DP in poly(vinyl butyral) and evaporation of the pigment was inhibited or eliminated. Both systems appeared to work equally well except during radiation exposure (See Section G). In that test, the Cymel-crosslinked poly(vinyl butyral) failed so badly that we believe something must have gone wrong in the test. (Perhaps the sample was not in contact with the cooling block.) This coating should be retested, but meanwhile, coatings of PJ 113 (391-15-170) perform quite satisfactorily.

TABLE V. THE EFFECT OF PURIFICATION METHOD ON PHYSICAL PROPERTIES OF DIOCTADECYL PHOSPHITE

Sample	Melting Point °C	Freezing Point °C	Index of Refraction at 59°C
Recrystallized from petroleum ether	52.5 to 53	52	1.4417
Recrystallized from alcohol	52.5 to 53	51.5	1.4423
Zone-refined	53.5 to 54	53	1.4398
Zone-refined and recrystallized	55.5 to 56.2	54	1.4382

D. Thermal Cycling Studies

A simple device that automatically cycles a phase-change coating above and below the phase-change temperature while the coating is maintained in a vacuum of 10^{-6} torr was designed and built for this program. The apparatus consists of a polished stainless steel plate to which are brazed two copper coils through which either a cold or hot fluid is circulated. The top of the plate is covered with a 12" diameter glass bell jar through which the sample can be viewed.

Thermal cycling was achieved by operating a pair of solenoid valves with an electric timer which simultaneously closed the hot valve and opened the cold valve and vice-versa on the next half-cycle. The hot fluid was a silicone oil maintained at 80°C while the cold fluid was tap water.

The timer was set to provide one full cycle every six minutes (three minutes heating--three minutes cooling) and to trip a counter on each cycle. Extreme plate temperatures were 27°C to 62°C and the samples were

thermally coupled to the plate with silicone grease. The heating and cooling rates are shown below:

	1st Minute	2nd Minute	3rd Minute
Heating rate	14°C/min	13°C/min	8°C/min
Cooling rate	23°C/min	11°C/min	1°C/min

The greatest limitation of this system lies in the fact that for the coatings investigated, few recover fully in this time period. Furthermore, the most likely cause of failure of the coatings investigated is vaporization of the pigment in a vacuum rather than actual failure due to cycling per se. A schematic diagram of the apparatus is shown in Fig. 7.

It became evident during thermal cycling studies that some sort of protective outer layer would be required to inhibit evaporation of pigments during prolonged exposure in space. Even dioctadecyl phosphite, which probably has the lowest vapor pressure of any of the pigments studied, will eventually evaporate in vacuum if not protected. At 50°C dioctadecyl phosphite has a vapor pressure of about 10^{-5} torr as measured with a Knudsen cell[3]. The dependence of vapor pressure on temperature is shown in Fig. 8.

Experimental Results - While about fifty samples were exposed to this test, many failed so completely that optical measurements "before" and "after" were unnecessary. Those that were measured are reported in Appendix B.

E. Recovery Kinetics

Phase-change coatings operate by the reversible dissolution and reprecipitation of the pigment as a function of temperature. While it was originally assumed that the precipitation or crystallization would occur at a particular temperature or at least over a very narrow temperature band, it soon became evident that this range of temperature is quite large and, furthermore, that the recovery rates at the various temperatures are dependent on the thermal history of the sample.

In order to determine quantitatively the rate of crystallization, or more important, the rate of change of transmission, a series of experiments were conducted on a model coating of dioctadecyl phosphite (DP) in poly(vinyl butyral).

The apparatus used in this experiment is pictured schematically in Fig. 9. It consists of a double-beam spectrometer in which a cylindrical sample cell is mounted. The cell is equipped with inlet and outlet tubes for

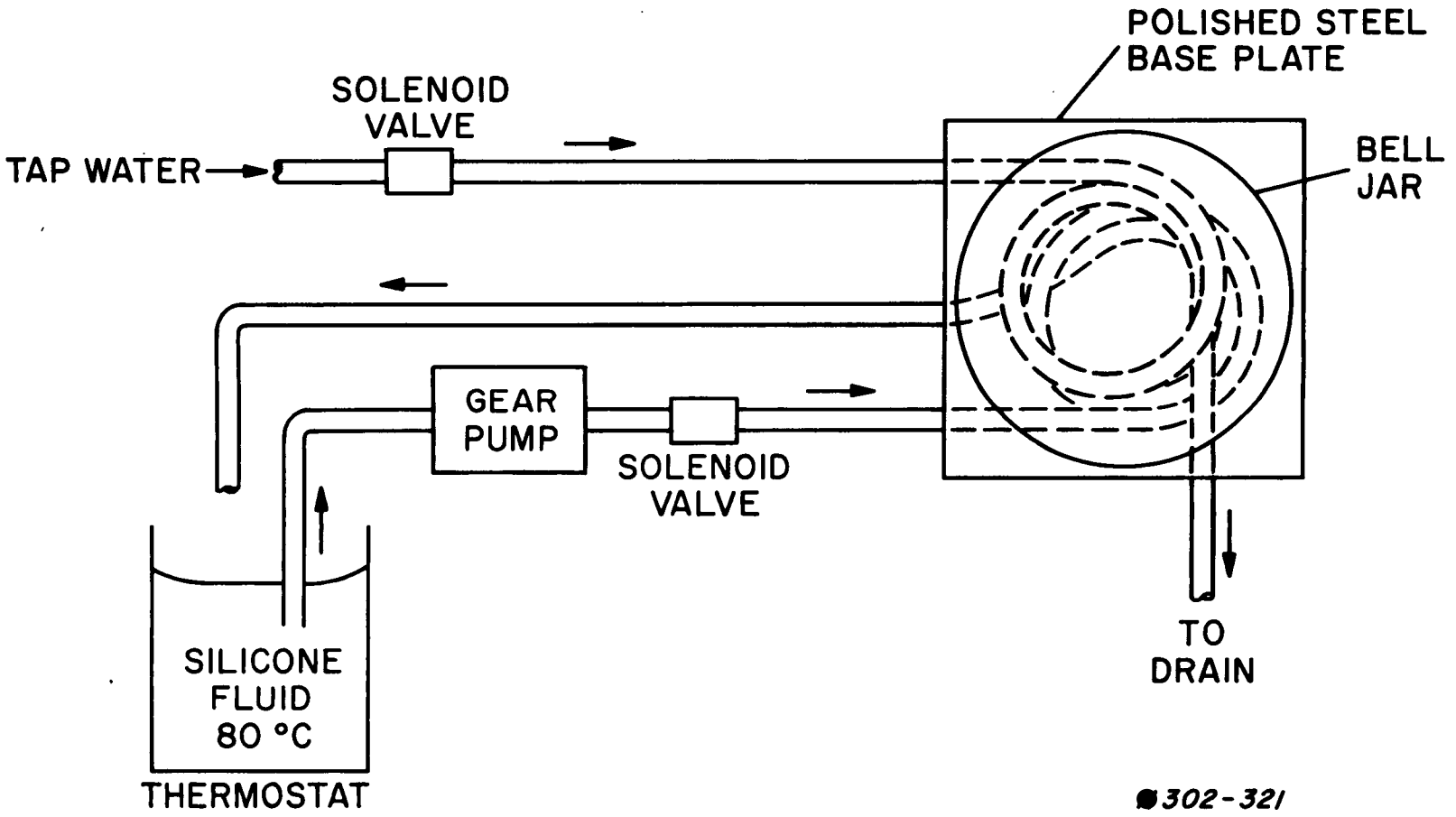


Figure 7. Thermal Cycling Apparatus

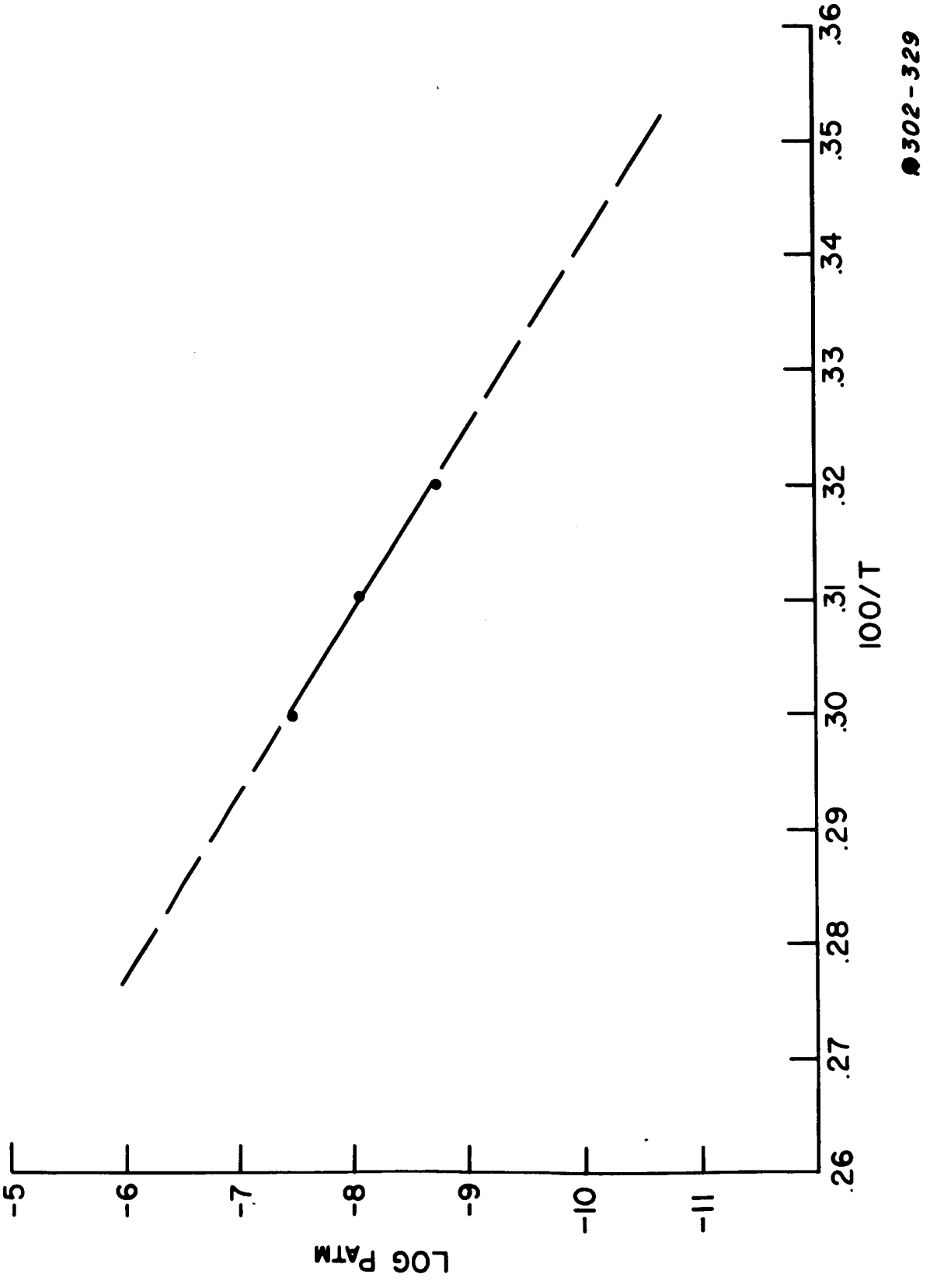
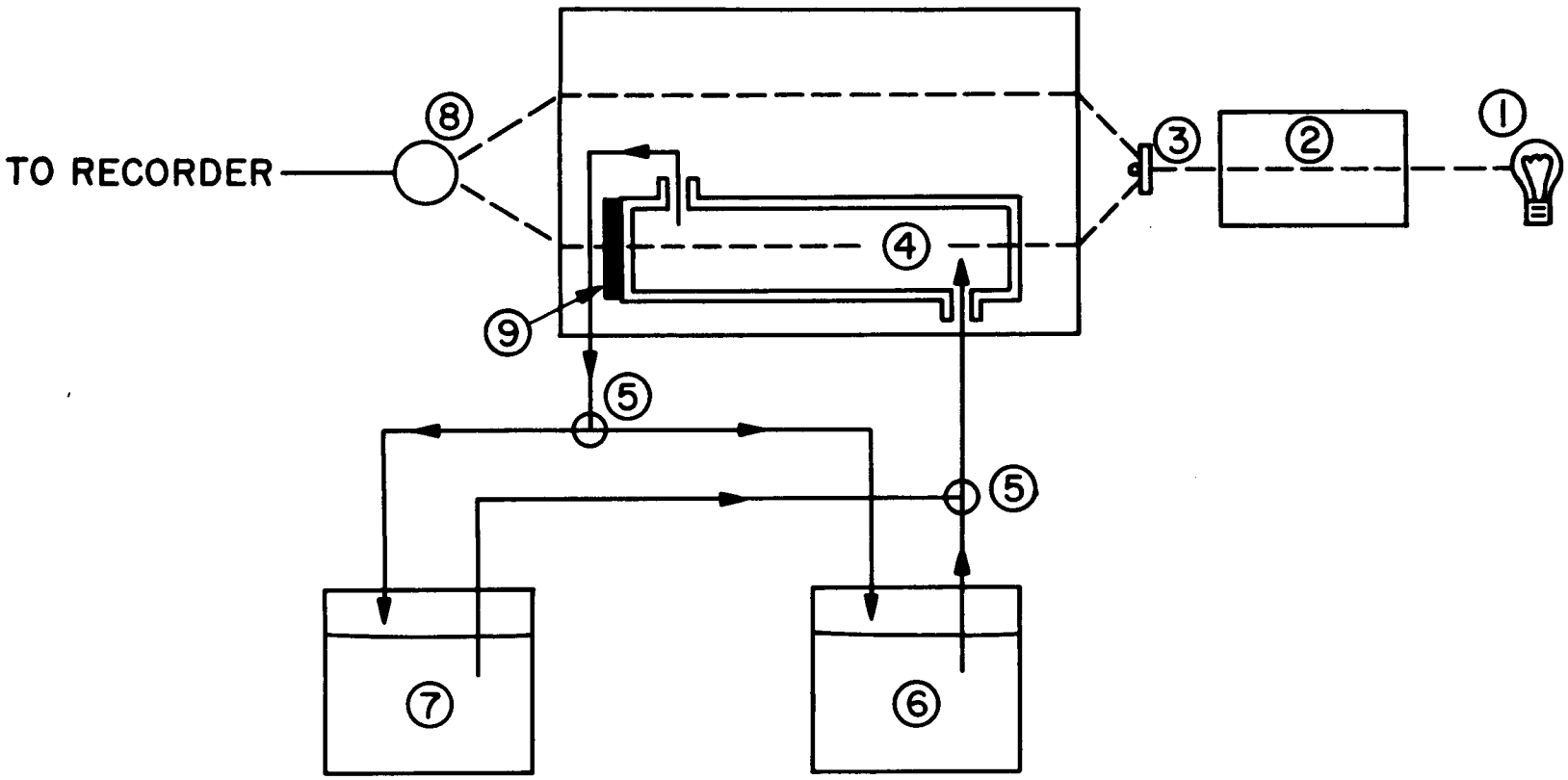


Figure 8. Vapor Pressure of Dioctadecyl Phosphite



1. LIGHT SOURCE
2. MONOCHROMATOR
3. BEAM SPLITTER
4. CYLINDRICAL QUARTZ CELL
5. THREE-WAY VALVE
6. LOW-TEMPERATURE THERMOSTAT
7. HIGH-TEMPERATURE THERMOSTAT
8. PHOTOMULTIPLIER
9. SAMPLE COATING ON CELL WINDOW

N302-322

Figure 9. Apparatus for Measuring Change of Transmission of Coatings with Temperature

thermostated water. The coating was sprayed directly onto the exterior surface of the cell window.

The experiments conducted in this apparatus varied significantly in the specific conditions being evaluated but all essentially consisted of heating the coating to some controlled elevated temperature and allowing it to attain equilibrium. The coating was then rapidly cooled (less than 1 minute) to some lower temperature and the change of transmission with time was recorded.

The change in transmission with time for a coating of DP in poly(vinyl butyral) at four different temperatures is shown in Fig. 10. The sample was in all cases heated to 62°C and then rapidly cooled to the specified temperature. It is apparent that the initial (0-10 minute) rate of crystallization (change in percent of maximum transmission) is essentially independent of temperature and quite rapid. It was also observed that at temperatures below about 42°C, not only were the initial rates comparable, but the entire rate curves matched. The equilibrium transmission was also found to be temperature-dependent in the range of 42 to 62°C.

This same coating, however, if heated to 65°C and allowed to recover at some lower temperature, shows a much slower rate of change of transmission. This is clearly shown in Fig. 11 where the change in transmission at about 40°C is shown for a coating heated once to 65°C and later to 60°C.

This behavior may be explained by the effect of temperature on nucleation sites. These sites exist at temperatures below 62°C, and result in rapid crystal growth when the sample is cooled sufficiently to precipitate the pigment. However, if these sites have been destroyed (presumably above 65°C) the rate of growth is severely restricted. It is interesting to note that if these nucleation sites are present, no simple kinetic order can be assigned to the rate of change of transmission. If these sites are destroyed, however, the initial change seems to follow first-order kinetics.

Another unexplained, though important, phenomenon concerns the difference in behavior between the DP purified by recrystallization and that which was further purified by zone-refining. Figure 12 shows a curve of the equilibrium absorbance of these two pigments in Butvar plotted against reciprocal absolute temperature. It is readily apparent that the zone-refined sample exhibits a change of transmission over a lower and broader temperature range. The limited kinetic data also indicate that the recovery rate at any temperature is greater for the zone-refined pigment than for the other. The use of this pigment should provide a coating exhibiting almost a continuous change in α_s with temperature over the range of 30 to 55°C.

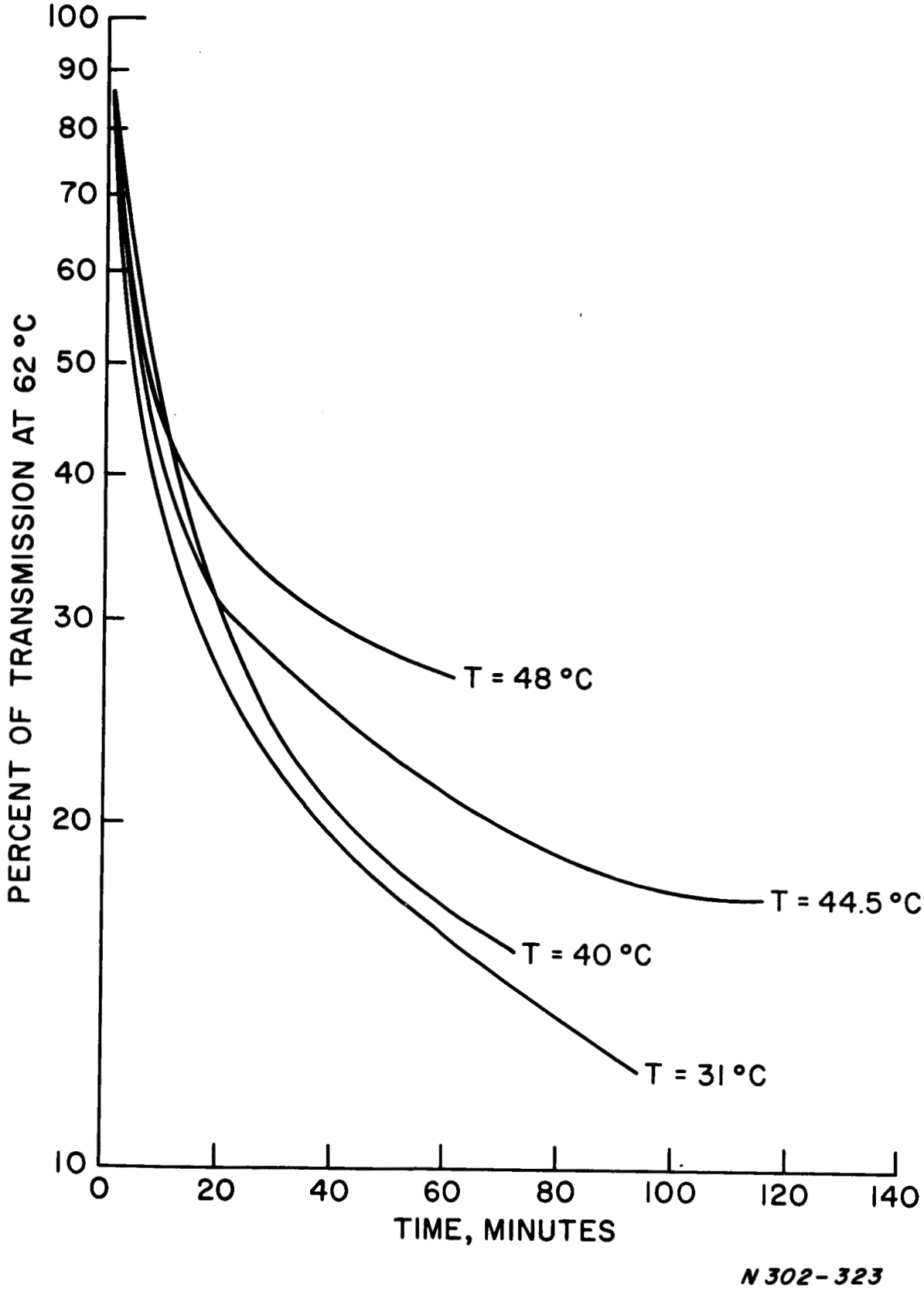


Figure 10. Rate of Change in Transmission of Coatings of DP in Poly(vinyl butyral) on Rapid Cooling from 62°C

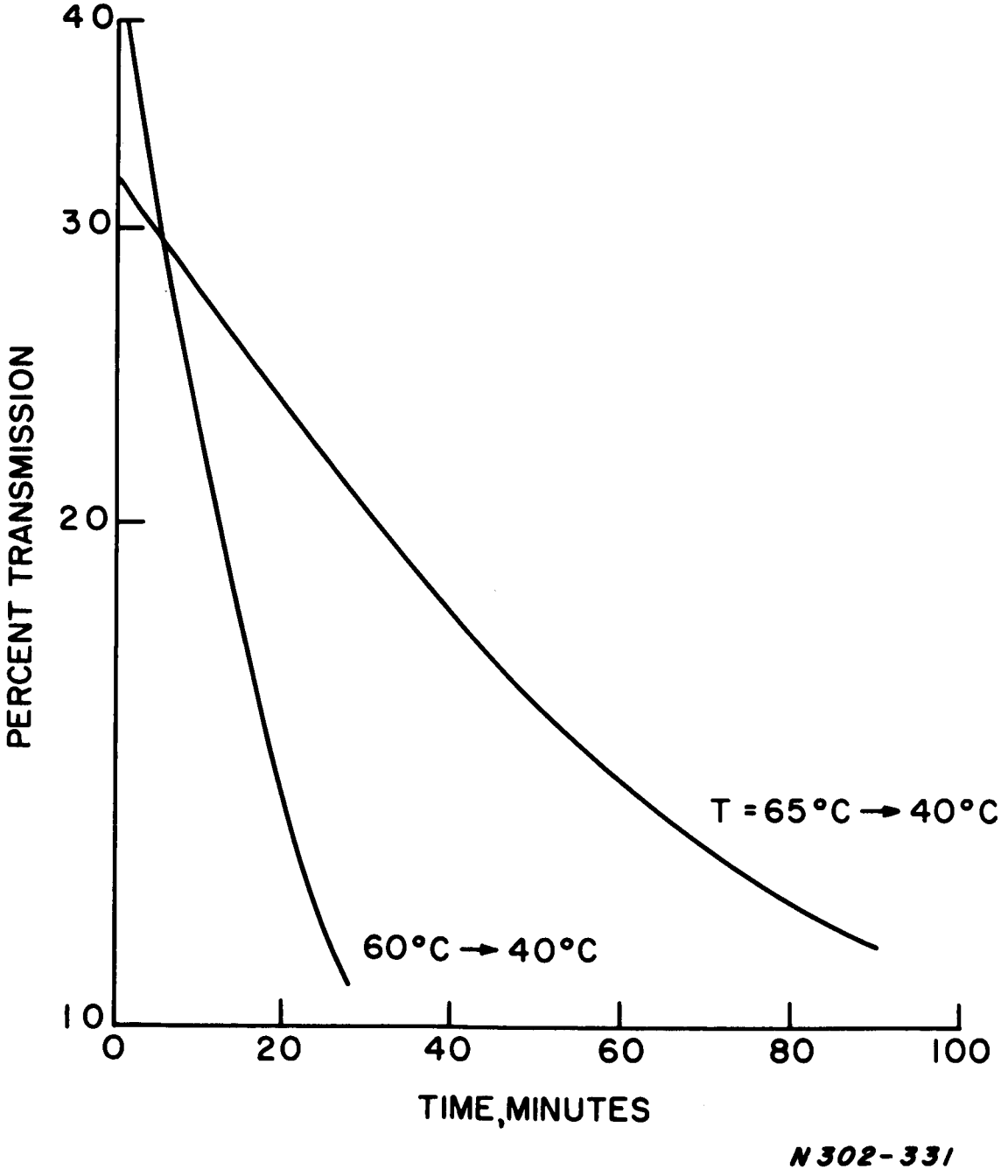


Figure 11. Rate of Change in Transmission of a Coating of DP in Poly(vinyl butryal) at 40°C after Heating to Higher Temperatures

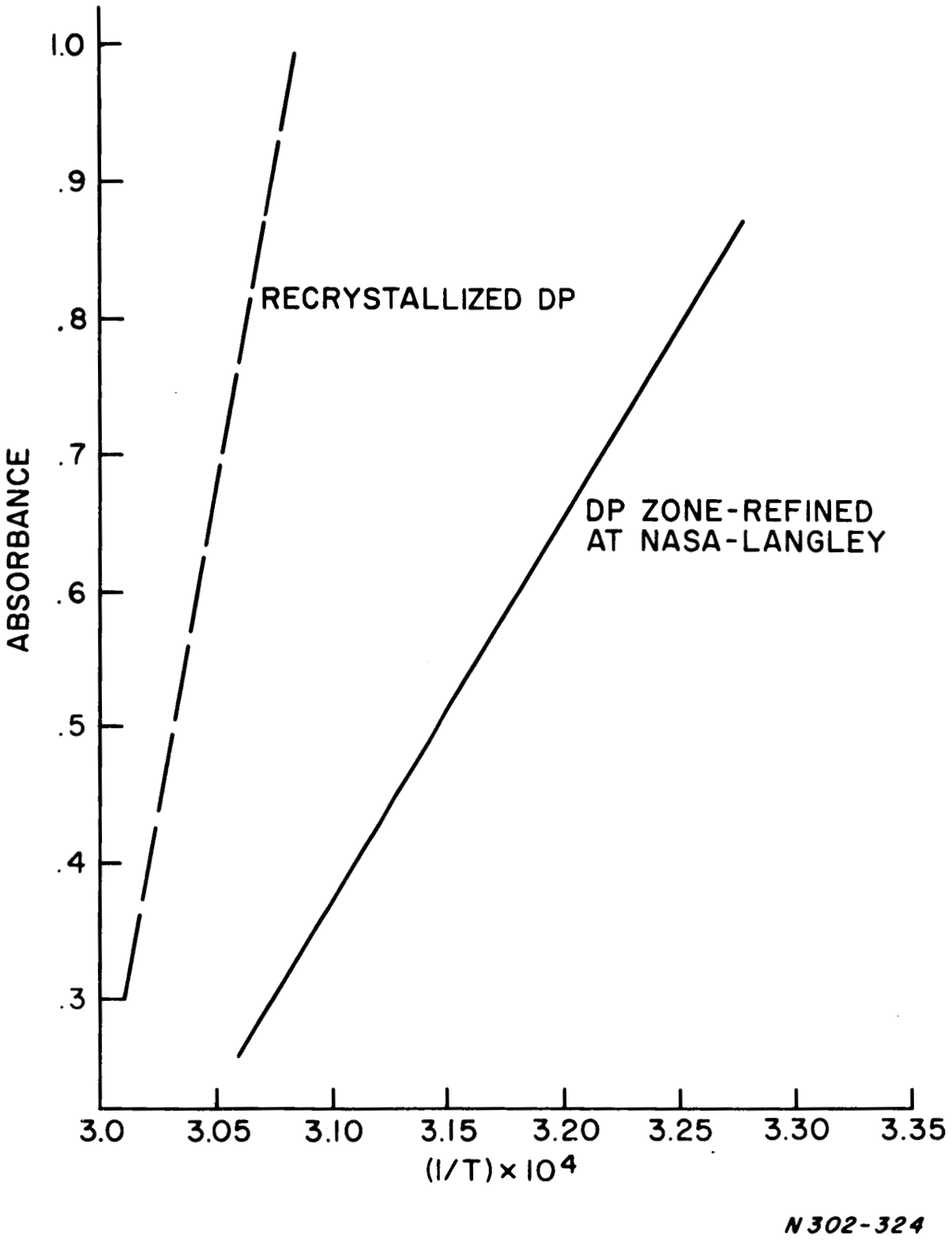


Figure 12. Absorbance vs. Temperature as a Function of Purification of Dioctadecyl Phosphite

F. Measurement of Optical Properties

1. Measurement of Optical Properties as a Function of Temperature

The successful operation of phase-change coatings requires that the reflectance in the solar region (0.2 to 2.0 microns) be temperature-dependent. Four different pieces of apparatus were used throughout the conduct of the program to measure this property: a calorimetric emissometer, a double beam spectrophotometer, a Gier Dunkel absolute directional reflectometer, and a Gier Dunkel portable solar reflectometer.

The use of the calorimetric emissometer for measuring the α_s/ϵ ratio as a function of temperature is described in Section F2. The use of this apparatus was limited to relatively few samples, since such experiments are very time-consuming compared to those conducted by other means. It is, however, the measurement that most closely approximates the end-use of the coating.

The continuous measurement of transmission as a function of time and temperature in a double beam spectrometer is described fully in Section E. While this is not a direct measurement of the property of interest (α_s), it did provide data relevant to the kinetics of solution and recrystallization.

The Gier Dunkle absolute directional reflectometer was modified to permit controlled heating of the sample. This instrument was coupled to a Perkin Elmer Model 99 monochromator for making spectral reflectance measurements in the wavelength interval from 0.28 to 2.0 microns. The Gier Dunkle portable solar reflectometer was used extensively to measure total solar reflectance. Though intrinsically not as accurate as the other techniques, the relative speed and ease of operation of the latter made its use attractive for this program.

The initial hypothesis of the mechanism of operation of phase-change coatings assumed that the reflectance was temperature-dependent, and that essentially there were only two temperature ranges to consider--that above which the coating was transparent and that below which it was opaque. This approach completely neglected the influence of crystallization rate and prior thermal history on the reflectance at any temperature. Since these parameters were not always stringently controlled, many of the measurements reported should be considered as indicative rather than as true performance evaluations.

A particular case in point is a series of measurements where the sample (DP in poly(vinyl butyral)) was slowly heated from room temperature to above 60°C and spectral reflectance was recorded at 5°C intervals. The sample was then allowed to cool and reflectance was again recorded at 5°C intervals. The resulting curve as plotted in Figure 13 might lead one to the conclusion that hysteresis occurs in phase-change coatings. A better

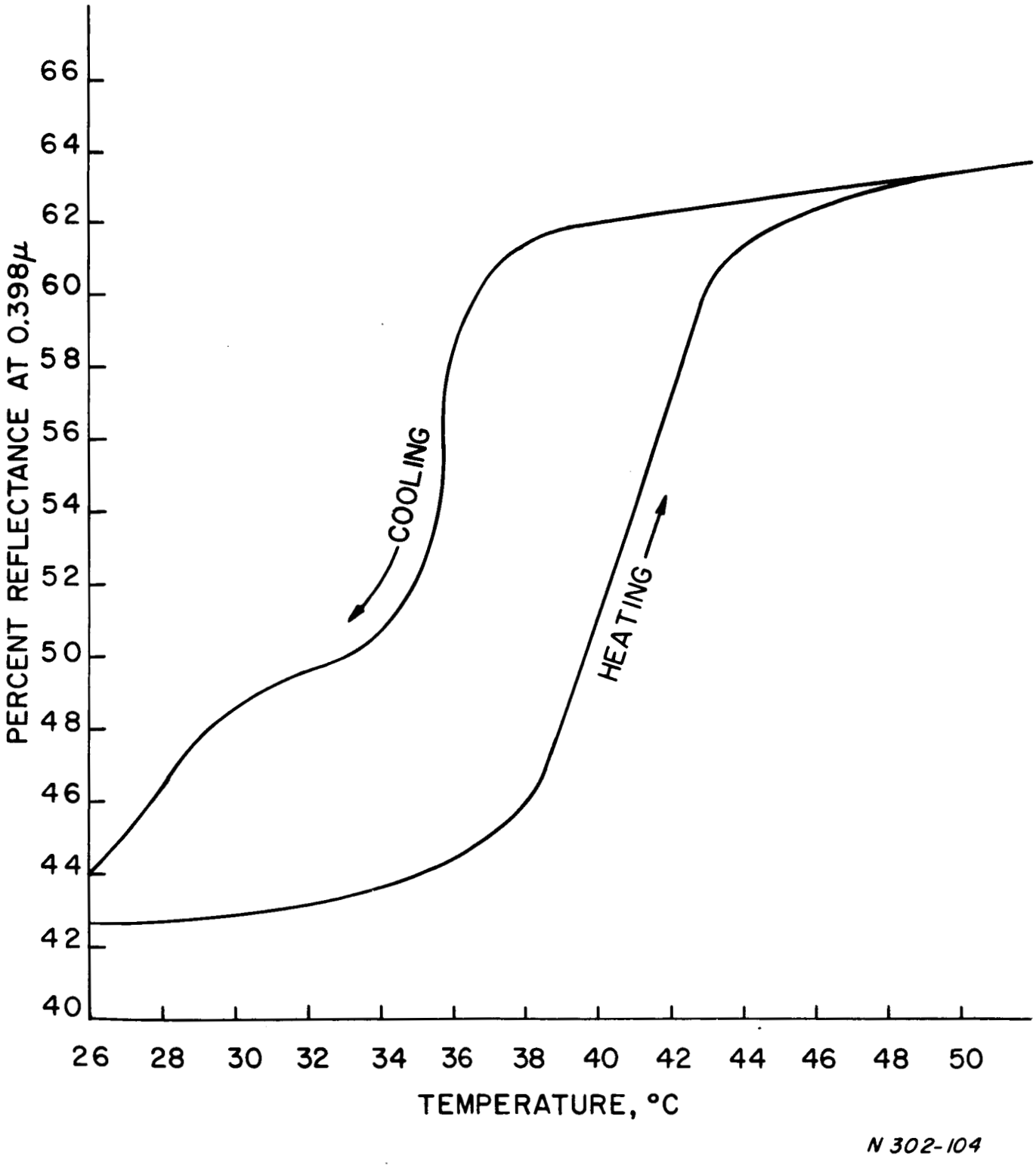


Figure 13. Apparent Temperature-Dependence of Optical Properties of DP in Poly(vinyl butryal)

explanation for this behavior was, however, established after the kinetics studies were completed and it was found that the recrystallization rate is extremely slow if the temperature has exceeded 62°C. It was established that even though thermal equilibrium had been achieved, the reflectance remained high, regardless of the temperature, for much longer periods of time than were allotted (cooling rate approximately 10°C/hr). This same phenomenon applies to the rate of solution as well. This further invalidates the data as presented, since it is possible that higher reflectance at the lower temperature could have been measured had we extended the time that the sample remained at any one temperature.

The data obtained from samples where the temperature was held constant for long periods of time and the total spectrum scanned are believed to be much more valid representations of the behavior of these coatings. Curves for the room temperature and elevated temperature reflectance for typical coatings of DP in poly(vinyl butyral) and erucic acid in poly (vinyl butyral) are shown in Figures 14 and 15.

Several experiments were conducted to measure the extent of variability in radiative properties that could be achieved by either changing pigment concentration or thickness.

A series of samples consisting of 150% erucic acid in poly(vinyl butyral) was prepared and measured on the portable reflectometer. The results are shown in Table VI.

TABLE VI. VARIATION IN SOLAR ABSORPTANCE OF ERUCIC ACID/BUTVAR AS A FUNCTION OF THICKNESS

Thickness, mils	Absorptance	
	Room temperature	Elevated temperature
1.5	.25	.15
5.6	.32	.17
11.2	.34	.17
12.9	.34	.18
13.8	.37	.17

The results of another series of experiments involving variations in the percentage of DP in RTV 602 are reported in Table VII.

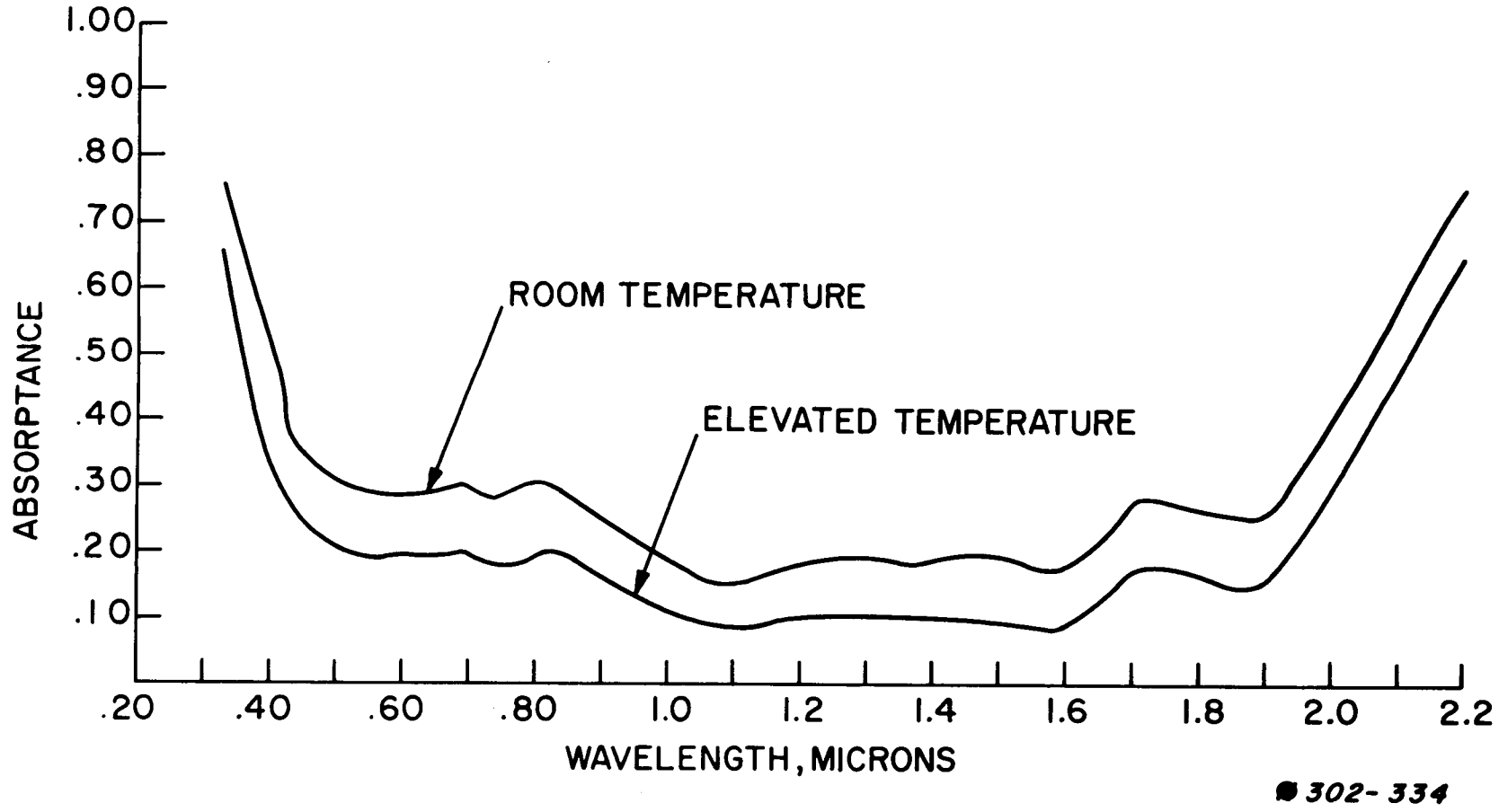


Figure 14. 20% Dioctadecyl Phosphite in Butvar, Room Temperature α_s = .33, Elevated Temperature α_s = .23

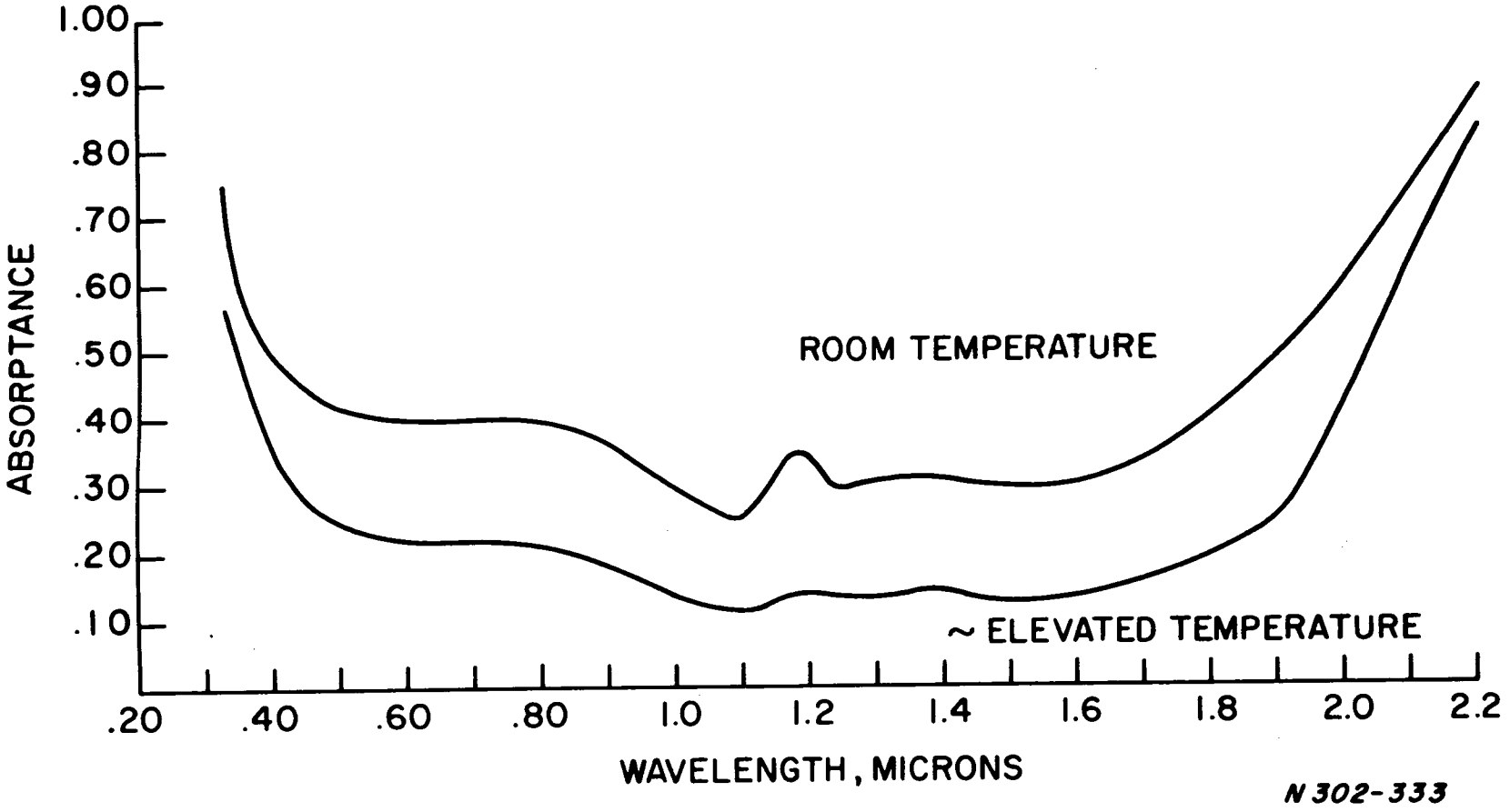


Figure 15. 150% Erucic Acid in Butvar, Room Temperature α_s = .44, Elevated Temperature α_s = .27

TABLE VII. VARIATION IN SOLAR ABSORPTANCE OF DP IN RTV 602 AS A FUNCTION OF PIGMENT CONCENTRATION

Concentration, %	Absorptance	
	Room temperature	Elevated temperature
2	.24	.16
3	.27	.16
4	.29	.17
5	.30	.18

2. Calorimetric Measurement of Solar Absorptance/Emmitance Ratio

The advantage of a phase-change thermal control coating over the more conventional passive coating is that at some elevated temperature the former rejects a significantly larger percentage of solar energy than it did at lower temperature, thereby preventing overheating. In order to demonstrate that the coating actually functions in this manner, a measurement of the α_s/ϵ ratio as a function temperature was made.

This measurement is most readily accomplished in the calorimetric emissometer. The appartus is essentially a cryogenic vacuum chamber designed for making calorimetric determinations of solar absorptance and hemispherical emittance. The apparatus, shown schematically in Figure 16 consists of a ferris wheel sample arrangement rotatable from outside the system and capable of supporting eight specimens in the chamber at one time. Each sample is suspended from an arm in a separate enclosure and can be rotated to face a quartz window through which the coating can be irradiated with a xenon lamp as a solar simulator. The specimen assembly pictured in Figure 17 consists of two copper plates sandwiched over a mica wound heater. The sample is equipped with two thermocouples to measure the temperature at each face, and is instrumented to measure electrical power input.

The coating used was a 10-mil film containing 1.5 parts erucic acid to 1.0 part Butvar over vapor-deposited aluminum. This particular coating exhibits little dependence of α_s on temperature below 53°C. However, having undergone a phase change, it remains transparent for a considerable period of time at temperatures as low as 45°C.

The experiment was divided into two portions, the first of which was to establish that the emittance was not temperature-dependent. This was accomplished by providing electrical power to the sample and measuring voltage,

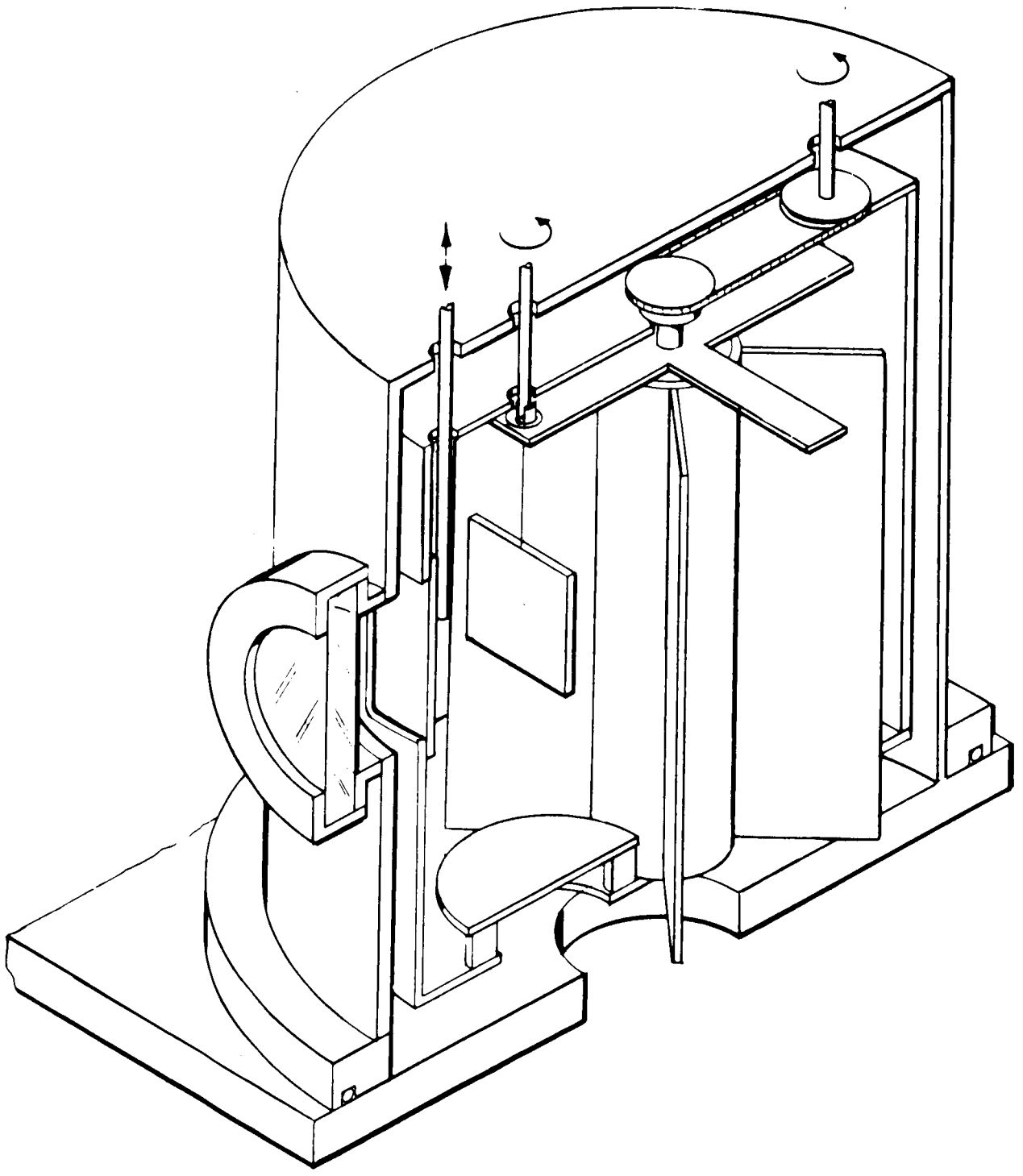


Figure 16. Calorimetric Emissometer

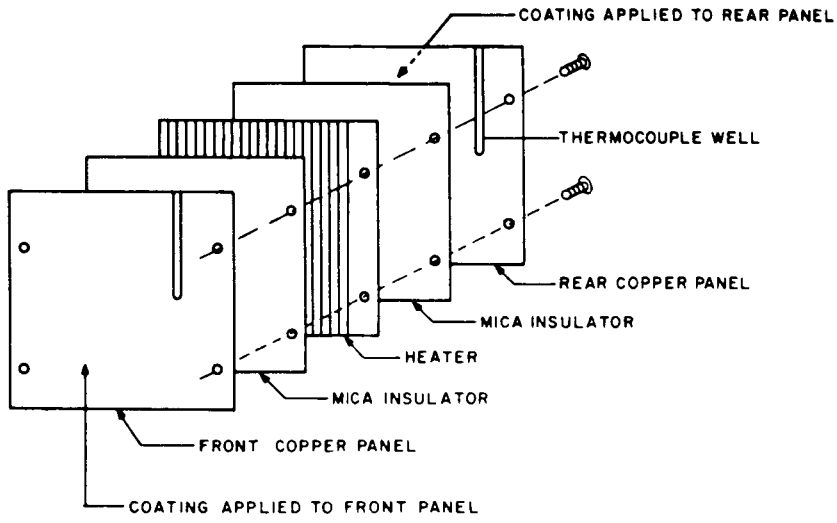


Figure 17. Calorimetric Emissometer Specimen Design

current and temperature. A plot of power vs T^4 (Figure 18) resulted in a straight line, proving that emittance is constant at and below the phase-change temperature.

The second phase of the experiment involved using a light source outside the chamber and irradiating the sample with a constant intensity. By adjusting the electrical power, the sample was brought to 52°C, or just below the phase-change temperature. The amount of radiation absorbed from the lamp at this temperature was calculated from a knowledge of the sample emittance and the electrical power input (approximately $3.3 \times 10^{-2} w/cm^2$). A slight increase in heater power was sufficient to raise the temperature to the phase-change point, resulting in a decrease in absorbed light to $2.5 \times 10^{-2} w/cm^2$ and an equilibrium temperature of 47°C. At this temperature, the recrystallization rate is so slow that the sample remains essentially transparent. In order to establish the temperature vs. power curve, additional points were obtained at higher power levels. The upper curve in Figure 19 shows what the thermal history would have been had the sample not undergone a phase-change at 53°C.

The experiment showed that α_s went from about 0.45 while opaque, to about 0.34 while transparent. The slowness of recovery at the lower temperature is responsible for the coating not cycling between these two temperatures within the time span of the experiment.

G. Irradiation of Phase-Change Coatings

Samples of finished phase-change coatings were irradiated in vacuum in the system described in Section B and shown in Figure 1. The first sample consisted of 33% dioctadecyl phosphite and 20% Resoflex R296 in poly (vinyl butyral) (Butvar B98). A protective layer of poly(vinyl butyral) cross-linked with Cymel 300 was applied and the coating baked 30 minutes at 75°C. This sample was placed in the vacuum system, and the system evacuated to 5×10^{-7} torr. The copper block behind the sample was heated to 100°C for ten minutes. Irradiation was started at 5 times solar intensity and 0.5 Mrad x-ray per hour. The pressure rose to 5×10^{-6} torr within an hour. Irradiation was stopped until the pressure fell again to 5×10^{-7} torr. Several more attempts at irradiation led to excessive pressure rises, so intensities were reduced to 2.5 times solar and 0.25 Mrad x-rays per hour. After 1000 equivalent sun-hours and 10^8 rads x-radiation (13 days elapsed time) the sample was removed from the vacuum system for measurement of its absorptance. The coating was badly discolored and appeared to have lost most of its pigment. Absorptance measurements confirmed this belief. Before irradiation the low- and high-temperature values were 0.36 and 0.21; after irradiation they were 0.29 and 0.24 respectively. The cause of this failure was not immediately obvious. Either the coating was much less stable than had been expected or it had not been in contact with the cooling block and had been grossly overheated by the high intensity light.

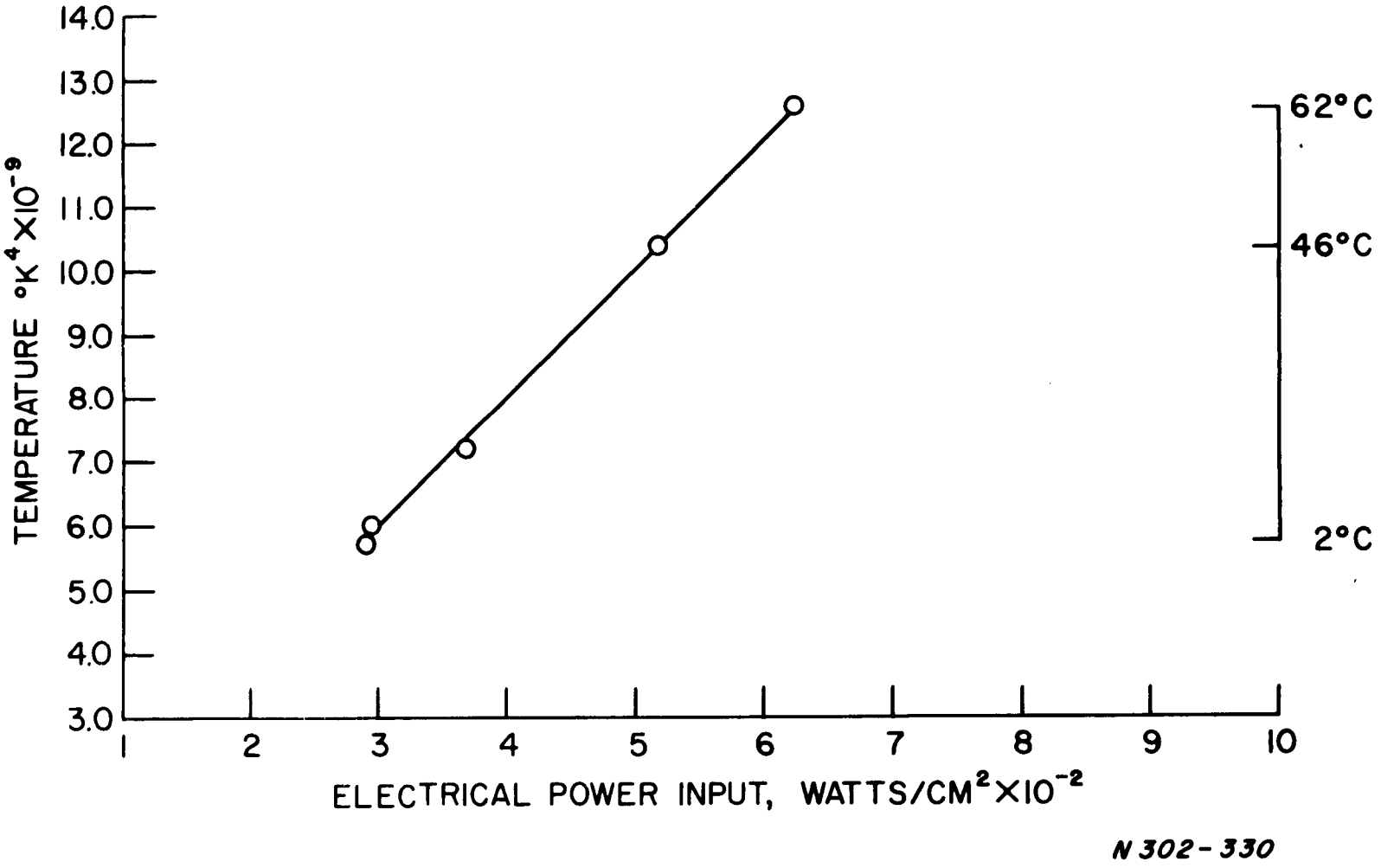


Figure 18. Plot Demonstrating Constant Emittance of Sample of 150% Erucic Acid in Butvar

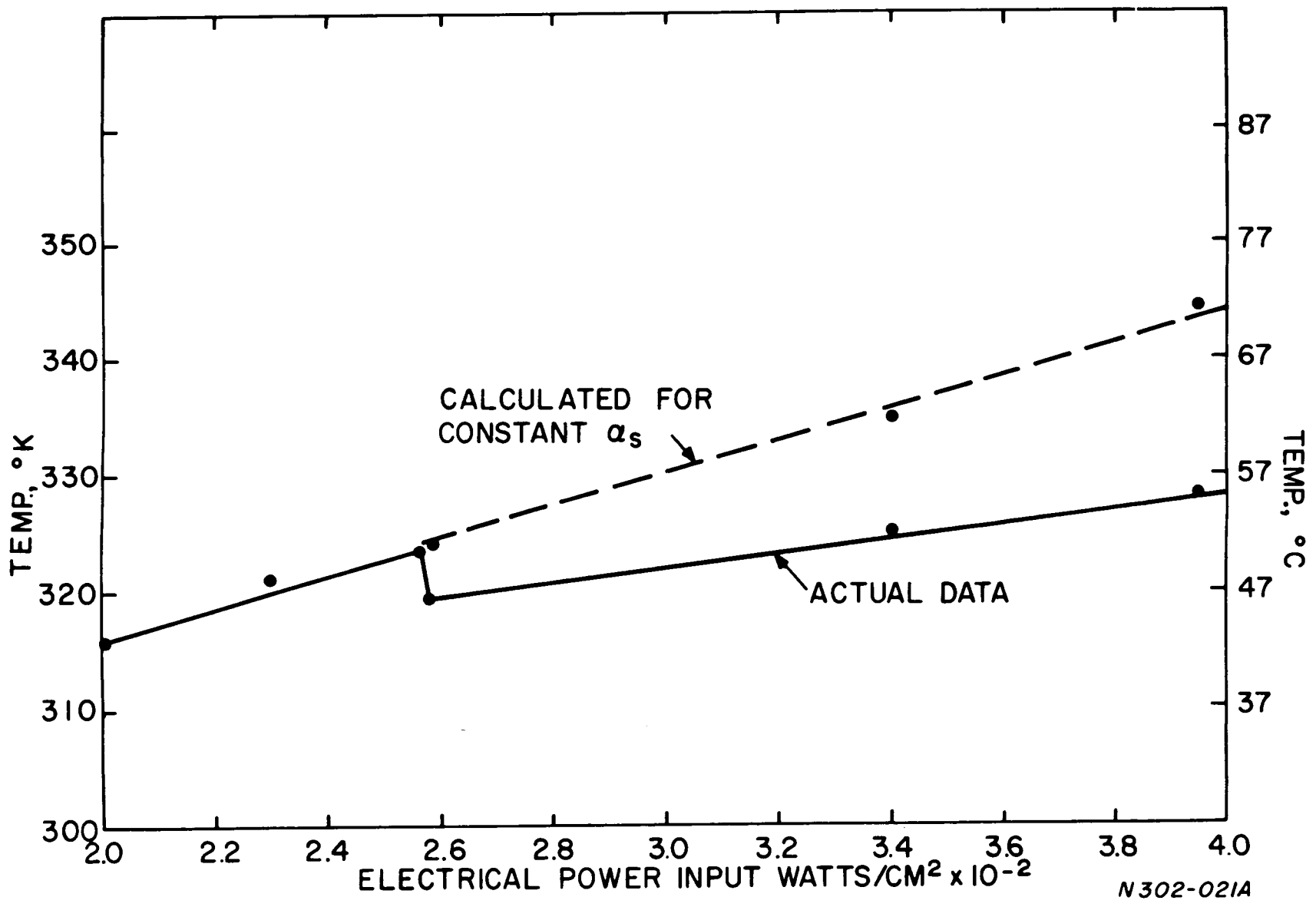


Figure 19. Effect of Phase-Change on Thermal Balance of Erucic Acid in Butvar

A second sample was clamped directly to the cooling block before the vacuum system was closed. This sample was the same as the first except that the protective coating was silicone 391-15-170 (PJ113). In this experiment the system was evacuated initially to 1×10^{-7} torr. The sample was heated to 100°C for ten minutes, then cooled to 25°C. Irradiation was started at 5 times solar and 0.5 Mrad x-ray per hour. A pressure rise to 1.5×10^{-7} torr was noted, but the pressure slowly fell to 5×10^{-8} torr. Upon completion of irradiation (1000 equivalent sun-hours and 10^8 rads) the sample was removed and its absorptance measured. The low- and high-temperature values of absorptance were 0.37 and 0.18 respectively.

A third sample, consisting of 33% dioctadecyl phosphite and 33% Resoflex R296 in poly(vinyl butyral) (Butvar B98) with a protective coating of silicone 391-15-170 (PJ 113), was irradiated in similar fashion. In this case, however, after ten minutes at 100°C, the sample was held at 40°C for the remainder of the experiment. Irradiation was conducted at 5 times solar and 0.5 Mrad per hour. A maximum pressure of 8×10^{-7} torr was reached before a slow decline began to 2×10^{-8} torr. The low- and high-temperature absorptances of the sample were 0.33 and 0.18. Before irradiation the low-temperature absorptance had been 0.34.

The good results obtained with the second and third samples lead us to believe that the first sample must not have been in contact with the cooling block and must, therefore, have been grossly overheated. The result obtained, then, should not be taken as evidence that the Cymel protective layer is unsatisfactory.

IV. CONCLUSIONS

A phase-change coating system consisting of dioctadecyl phosphite in poly(vinyl butyral) has been developed which changes in α_s/ϵ ratio by about a factor of two between 25°C and 50°C. The reversible change in α_s/ϵ is stable through at least 10^3 thermal cycles in vacuum and is nearly unaffected by exposure in vacuum to 100°C for ten minutes, 1000 equivalent sun-hours of ultraviolet and 100 Mrad of x-ray. The coating can be applied either by brushing or spraying. When the coating is heated to 50°C, it changes from its high absorptance to its low absorptance form within seconds. Recovery of the high absorptance on cooling requires a period of minutes.

Coatings of stearic acid in poly(vinyl butyral) also provide reversible changes in α_s of about a factor of two, but since the phase-change temperature is slightly higher than the contractual requirements, extensive investigation of this system was not conducted.

Calorimetric measurements conclusively demonstrated the ability of phase-change coatings to operate as a self-thermostatic thermal control system.

In some systems, there is no unique "phase-change" temperature, but rather a constant change of absorptance with temperature over a range of at least 20°C. There is, however, a temperature at which the coating undergoes a rapid change in absorptance. In the best coatings this temperature is at or just below the melting point of the pigment.

Evaporation of the pigment in vacuum was shown to be a major concern for most phase-change coatings, leading to permanent changes in optical properties and possible contamination of neighboring surfaces. An effective method of preventing such evaporation was developed, making rates of evaporation unmeasurably low.

V. REFERENCES

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APPENDIX A

SUMMARY OF FORMULATIONS
(All percentage compositions are grams per 100 grams of binder)

A. COATINGS OF PJ113 OR SILICONE PRODUCTS DEPARTMENT 391-15-170

1. ~10%, 2,2'-Phenylimino diethanol - Slightly cloudy at room temperature. Transparent at 50°C.

2. Benzyl cinnamate - Transparent. Almost insoluble in resin.

3. 30% Dibutyltin dichloride - Opaque to 100°C.

4. 10%, 20% Dibutyltin dichloride - Transparent. Some samples did not cure.

5. 10% Pentite - Transparent, cracked. One sample showed possible low temperature change.

6. 2% Dioctadecyl phosphite - Good phase-change. α_s = .25 ← → .43. Some samples did not cure. After 10^3 cycles pigment had extruded to surface.

7. 10% Erucic acid - Cloudy, not very opaque. Very transparent hot.

8. 5%, 10% Triphenyl phosphite - Did not cure.

9. 10% Lauric acid - Slightly cloudy. Most of pigment on surface.

10. 10% Carbowax 1000 - Pigment agglomerates.

11. 10% Carbowax 20M - Pigment agglomerates.

12. 5% Fluorocarbon ether* - Semi-opaque. No phase-change.

13. 10% Tetradecanol - Opaque. Pigment on surface.

14. 10% 3-Methoxycatechol - Pigment agglomerates.

15. 2.5% Dioctadecyl phosphite - Permanently opaque after 10^3 cycles.

* 3 - [2-(heptafluorocyclobutyl)-hexafluorocyclobutyl] - 1, 2, 3-triethoxy-4, 4-difluorocyclobutene.

16. 5% Fluorocarbon ether* plus 10% tetradecanol - Most of ether evaporated during cure.

17. 10% Triphenyl silane - Transparent.

18. 20% Octamethyl cyclotetrasiloxane - Transparent. Pigment evaporated during cure.

19. 10% Pyrogallol - acetanilide eutectic. No phase-change.

B. COATINGS OF RTV-602

1. 20% Dibutyltin dichloride - Did not cure.

2. 10% Dibutyltin dichloride - Did not cure.

3. 20% Dioctadecyl phosphite - White, nearly opaque. Reversible phase-change. Did not get completely transparent.

4. 10% Dioctadecyl phosphite - Same as above.

5. 2% Dioctadecyl phosphite - α_s = .235 ← → .162.

6. 3% Dioctadecyl phosphite - α_s = .268 ← → .167.

7. 4% Dioctadecyl phosphite - α_s = .290 ← → .170.

8. 5% Dioctadecyl phosphite - α_s = .295 ← → .184.

9. 3% Triphenyl phosphite - Looked good before fully cured. After cure remained opaque to 100°C.

10. 10% Pyrogallol - acetanilide eutectic - Did not cure. Turned brown overnight.

C. COATINGS OF GLASS RESIN 650

1. 40% Tetraphenyl tin - Opaque to 90°C.

2. 40% Dioctadecyl phosphite - Phase change. Slow recovery.

3. 10% Erucic acid - Opaque due to frothy structure.

D. COATINGS OF POLY(VINYL FLUORIDE)

1. 20% Dioctadecyl phosphite - Brown.
2. 20% Erucic acid - Brown.
3. 20% Lauric acid - Brown.
4. 10% Perfluorooctyl adipate - Transparent.
5. 20% Perfluorooctyl adipate - Transparent. Pigment believed to have evaporated.

E. COATINGS IN SILICONE SR126

1. 40% Dioctadecyl phosphite - Some change at ~55°C. Remained slightly opaque to 70-80°C.
2. 30% Dioctadecyl phosphite - Phase-change but not very transparent. Too much pigment.
3. 20% Dioctadecyl phosphite - Similar to above.
4. 10% Dioctadecyl phosphite - White, opaque. Phase change good, but reversal slow.
5. 40% Tetraphenyl tin - No change below 100°C.
6. 40% Dibutyltin dichloride - No change to 150°C.
7. 10% Dibutyltin dichloride - Transparent.
8. 20% Dibutyltin dichloride - White, opaque. Reversible phase-change.
9. 30% Dibutyltin dichloride - Same as above, but less transparent.
10. 2% Triphenyl phosphite - Transparent.
11. 5% Triphenyl phosphite - Transparent.
12. 10% Triphenyl phosphite - Slightly opaque at 10°C. Pigment on surface.

E. COATINGS OF BUTVAR B-98

1. 20% Azelaic acid - Transparent
2. 30% Dibutyltin dichloride - Transparent
3. 30% Tetracosane - Little recovery after first cycle.
4. 30% Octadecanol - Little recovery after first cycle.
5. 50% Octadecanol - White, opaque. Little recovery after first cycle.
6. 30% Tetradecanol - Transparent.
7. 20-100% Erucic acid - Good phase change.
8. 20% Fluorocarbon ether* - Cloudy. No phase-change.
9. 10% Fluorocarbon ether* - Same as above.
10. 5% Fluorocarbon ether* - Transparent.
11. 10% 2-Nitrobiphenyl - Transparent.
12. 20% 2-Nitrobiphenyl - Transparent.
13. 2-20% 3-Methoxycatechol - Transparent.
14. 2-5% Perfluorooctyl adipate - Opaque. No phase-change.
15. 5-20% Triphenyl phosphite - Transparent.
16. 20-40% Benzyl cinnamate - Transparent.
17. 10-30% Lauric acid - Transparent.
18. 40% Lauric acid - White but spotty. Phase-change.
19. 10-20% Carbowax 1000 - Transparent.
20. 10-20% Carbowax 20M - Transparent.
21. 20% Triphenylsilane - Transparent.
22. 25% Pyrogallol - acetanilide eutectic - Turned brown at 70°C in minutes or in days at room temperature.

23. 25% Dioctadecyl phosphite recrystallized from pet. ether plus 0.25% Cab-O-Sil. - α_s = .19 to .35. Recovers in about 15 seconds.

24. 25% Dioctadecyl phosphite recryst. from pet. ether plus 1% 3-5μ quartz - α_s = .18 to .31.

25. 33% Stearic acid plus 1% Cab-O-Sil - α_s = .18 to .35. Recovers in few minutes, phase-change about 55°C.

26. 33% Dioctadecyl phosphite recrystallized from pet. ether, 20% dibutyl phthalate, 1% Cab-O-Sil - Not homogeneous. Plasticizer oozes.

27. 33% Dioctadecyl phosphite recryst. from pet. ether, 20% triphenyl phosphite, 1% Cab-O-Sil - Nearly transparent.

28. 50% Erucic acid, 20% dibutyl phthalate, 1% Cab-O-Sil - Phase-change at 55°C. Recovery in about an hour.

29. 50% Erucic acid, 20% triphenyl phosphite, 1% Cab-O-Sil. - No phase-change.

30. 33% Dioctadecyl phosphite, 20% Resoflex R296, 1% Cab-O-Sil (See "Formulations" section of main report.)

31. 33-50% Octadecanol, 10% Resoflex R296 - Phase-change. α_s = .33.

32. 33% Octadecanol, 20% Resoflex R296 - Destroyed by thermal cycling.

33. 33% Tetradecanol, 10-20% Resoflex R296 - Transparent.

F. COATINGS OF BUTVAR B-90

1. 20% Dioctadecyl phosphite - Opaque. Phase Change. Cloudy surface after 10^3 cycles. Transparent after wiping. Addition of Cab-O-Sil made little difference.

2. 30% Erucic acid - Phase change. Very transparent when warm.

3. 40% Benzyl cinnamate - Nearly transparent. No phase-change.

4. 30% 4-Methoxyacetophenone - Transparent.

5. 30% 1-Naphthylacetate - Transparent.

G. COATINGS OF BUTVAR B-76

1. 20% Dioctadecyl phosphite - Some phase change, but opaque in sections.

2. 30% Erucic acid - Phase-change. Very transparent warm.

3. 40% Benzyl cinnamate - Nearly transparent. No phase-change.

4. 30% 4-Methoxyacetophenone - Transparent.

5. 30% 1-Naththylacetate - Transparent.

APPENDIX B

THERMAL CYCLING EVALUATION
TABLE B-1

Sample Designation	Sample Description	Solar Absorptance Prior to Cycling RT	Prior to Cycling ET	After Cycling RT	After Cycling ET	Comments
17D	30% Erucic in B76+PJ113overcoat	.17		.18		20 hrs. after cycling
17G2	20% DP in B76+B90+1/4% Cab-O-Sil	.23		.21		20 hrs. after cycling
17L	25% DP in B90+1/4% Cab-O-Sil	.28	.15	.25		2 hrs. after heating α_s = .27
20E	25% DP-1/4% Cab-O-Sil in B98	.35	.19	.22		after several hrs. α_s=.33
20F	25% DP+1% quartz (3-5 microns) + B98	.31	.18			after several hrs. α_s=.30
Langley	50% Paraffin in 50% ethylene-vinyl acetate copolymer	.42		.30		
Langley	30% Paraffin in 70% styrene-vinyl toluene copolymer	.31		.27		
23A	33% DP + 1% Cab-O-Sil in B98	.36	.16			17 mils thick
23B	33% Stearic acid + 1% Cab-O-Sil in B98	.35	.18	.27		
23C	20E + PJ 113 overcoat			.31		
27A	33% DP +20% Resoflex R296 in B98 overcoated with B98 + Cymel 300	.34		.31	.21	
27C	33% DP + 20% Resoflex R296 in B98 overcoated with PJ 113	.32		.37	.19	
27E	33% DP + 33% Resoflex R296 in B98 overcoated with PJ 113	.32		.37	.19	

TABLE B-2. THERMAL CYCLING EVALUATION

Sample Designation	Sample Description	Solar Absorptance: Prior to Cycling, RT	Solar Absorptance: 225 Cycles in Air, RT	Solar Absorptance: 1000[1] Cycles in Vacuum, RT	Solar Absorptance: 20 Hrs. After Cycling, RT	Comment
23D	23A overcoated with RTV 602	.39	.38	.38	.39	Fast recovery
23E	23A overcoated with PJ 113	.35	.39[2]	.37[2]	.36	
23F1	20E	.39	.36	.40[3]	.40	
23F2	20E overcoated with RTV 602	.39	.37	.41[3]	.41	Fast recovery
23G	23A overcoated with RTV 602	.36	.33	.26	.33	
23H	23A overcoated with RTV 606	.38	.36	.30	.36	
23K	33% DP+20% dibutyl phthalate in B98 overcoated with PJ113	.44	.45	.41	.44	Fast recovery
23M	33% DP+20% triphenyl phosphite + 1% Cab-O-Sil in B98 overcoated with B76	.30	.31	.29	.34	Slow recovery
24D	33% DP+20% Resoflex R296+1% Cab-O-Sil in B98	.30		.25	.28	
24E	24D overcoated with Cymel 300	.32		.29	.31	
24F(a)	33% DP+10% Resoflex R296 in B98 overcoated with B98 and Cymel 300	.42		.44	.43	
24F(b)	33% DP+10% Resoflex R296 in B98 overcoated with B98 and Cymel 300	.41		.35	.37	
24G	Same as 24F; overcoated with PJ 113	.35		.38	.36	
24H	5% Octadecanol+10% Resoflex R296 in B98+Cymel 300	.35		.27	.30	
24N	24J overcoated with B98 + Cymel 300	.35		.35		
24M	24J overcoated with PJ113	.37		.32		
24J	33% Octadecanol+20% Resoflex in B98	.38		(sample destroyed in test; blistered, shrunk)		
24I	33% Octadecanol+10% Resoflex in B98	.33		.24		

(1) Measured within 20 minutes after cycling
(2) Sample appeared wavy
(3) Did not appear to be cycling in vacuum

APPENDIX C

LIST OF MANUFACTURERS OR SUPPLIERS OF IMPORTANT MATERIALS

"Glass Resin" -- Owens-Illinois

Silicone PJ113 or 391-15-170 -- General Electric Company, Silicone Products Department

"Butvar" poly(vinyl butyral) -- Monsanto Company

Dioctadecyl phosphite -- Hooker Chemical Corporation

"Cab-O-Sil" -- Cabot Corporation

"Resoflex" -- Cambridge Industries Company

"Cymel 300" -- American Cyanamid Company

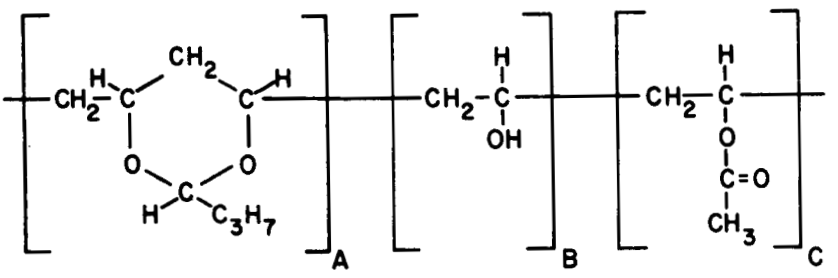
"Dalbon" poly(vinyl fluoride) -- Diamond Alkali Company

"Kynar" poly(vinylidene fluoride) -- Pennsalt Chemical Company

APPENDIX D

CHEMICAL STRUCTURES AND PHYSICAL PROPERTIES OF IMPORTANT MATERIALS

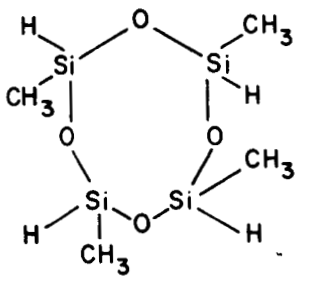
1. Poly(vinyl butyral)



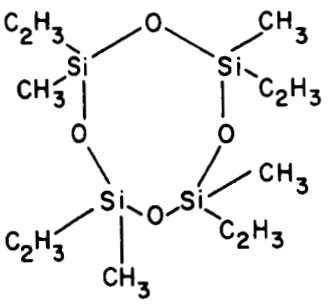
The proportions of A, B, and C are controlled and they are randomly distributed along the molecule. In Butvar B98, the proportions are 80%, 18-20%, and 0-2% resprectively.

2. Silicone PJ113 or 391-15-170

A condensation polymer of methyl hydrogen tetramer



and methyl vinyl tetramer



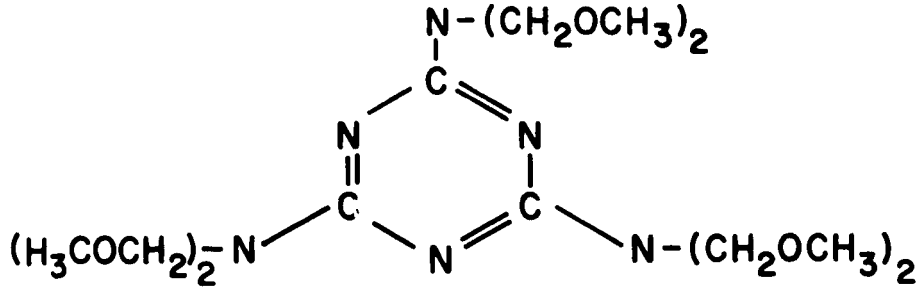
Cured films are hard, mar resistant, and non-yellowing even after exposure to intense ultraviolet radiation. They are recommended for use as protective coatings, as solvent barriers, and as means of improving the surface finish of other components.

3. Resoflex R-296

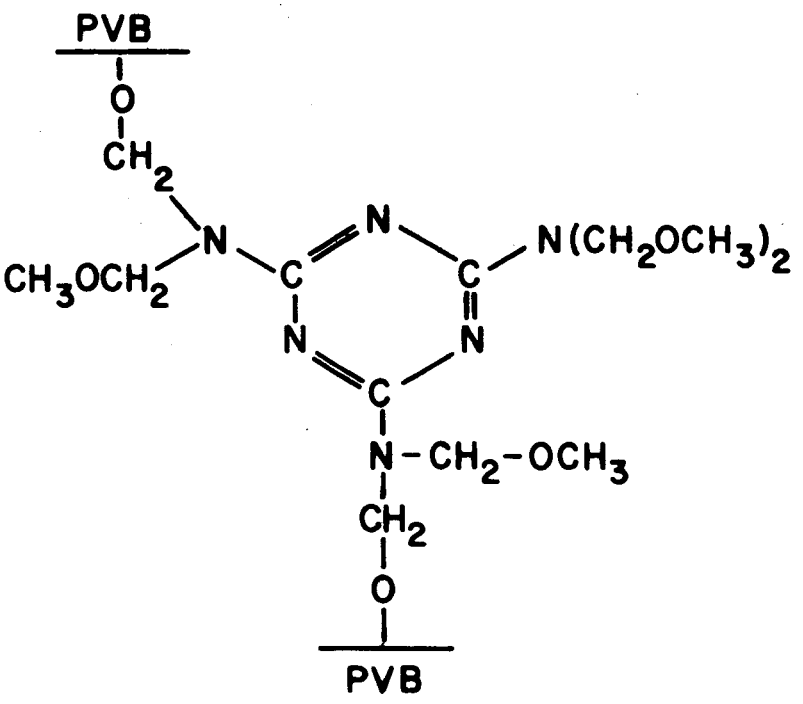
This plasticizer is a resinous, saturated alkyd whose exact chemical structure is not known. It is a pale liquid with a Gardner-Holt viscosity Z-2 and a refractive index of 1.471.

4. Hexamethoxymethylmelamine

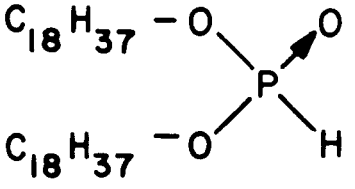
(Cymel 300)



Poly(vinyl butyral) can be cross-linked by reaction of hydroxyl groups with the melamine to give a structure which can be represented as:



5. Dioctadecyl phosphite



This material, used as a pigment, has a molecular weight of 586, melts at 55.5 to 56.2°C, freezes at 54°C, and has a refractive index $n_D^{59} = 1.4382$.